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MATHEMATICS

NEW ESTIMATIONS OF TRIGONOMETRICAL SUMS CONTAINING PRIMES

By I. M. VINOGRADOW, Member of the Academy

In my recent papers (1) I have developed a general method of estimation of sums of the form

$$S = \sum_{p \leqslant N} e^{2\pi i k f(p)},$$

where p runs over the sequence of primes. This method gives by certain conditions not trivial estimations in the case when $f(x)$ is a polynomial and in some other general cases when $f(x)$ is not a polynomial.

In the published theorems the estimation of the sum S (by certain conditions) has been given in the form

$$|S| \leqslant cN(\log N)^{-h},$$

where h is an arbitraty large constant > 1 and c is a constant depending on h. Such estimations are quite sufficient for the resolution of a large circle of problems of the theory of numbers (e. g. the additive problems with primes) (2).

Now by improvement of my method we can obtain more exact estimations of a new type. The following results are connected with the new estimations.

1. Let N be an integer > 0; p runs over the sequence of primes;

$$S = \sum_{p \leqslant N} e^{2\pi i a m p};$$

$$\alpha = \frac{a}{q} + \frac{\theta}{q^2}; \quad (a, q) = 1; \quad 0 < q \leqslant N; \quad |\theta| \leqslant 1;$$

$$Q = \min\left(q, \frac{N}{q}\right);$$

m is an integer; $0 < m \leqslant Q^{\frac{1}{3}}$.

Then we have

$$|S| \leqslant c_1 N Q^{-\frac{1}{6}+\varepsilon} \log N,$$

where ε is an arbitrary small positive constant and c_1 is a constant.

In particular by $m = 1$ we have

$$|S| \leqslant c_1 N Q^{-\frac{1}{4}+\varepsilon} \log N.$$

Example. Let H be an integer > 0. Then we have

$$\left| \sum_{p \leqslant H^2} e^{2\pi i \frac{p}{H}} \right| \leqslant c_1 H^{2-\frac{1}{4}+\varepsilon}.$$

2. Let N be an integer >0; p runs over the primes of the interval $0<p\leqslant N$;

$$\alpha=\frac{a}{q}+\frac{\theta}{q^2};\ (a,\ q)=1;\ 0<q\leqslant N;\ |\theta|\leqslant 1;$$

$$Q=\min\left(q,\ \frac{N}{q}\right).$$

Then, for any ρ $(0<\rho\leqslant 1)$, the number of values of the fraction

$$\{\alpha p\}\ \text{(we put } \{z\}=z-[z])$$

satisfying the condition

$$0\leqslant\{\alpha p\}\leqslant\rho$$

may be expressed by the formula

$$\rho\pi(N)+O\left(N(\log N)^2Q^{-\frac{1}{6}+\varepsilon}\right).$$

Example. Let H be an integer >0; p runs over the primes of the interval $0<p\leqslant H^2$.

Then the number of values of the fraction

$$\left\{\frac{p}{H}\right\}$$

lying in the interval

$$0<\left\{\frac{p}{H}\right\}\leqslant\rho$$

may be expressed by the formula

$$\rho\pi(H^2)+O\left(H^{2-\frac{1}{6}+\varepsilon}\right).$$

3. Let N be an integer >0; p runs over the sequence of primes;

$$S=\sum_{p\leqslant N}e^{2\pi imf(p)};$$

k is a constant integer >1;

$$f(p)=\alpha p^k+\ldots+\alpha_k;\ \alpha,\ \ldots,\ \alpha_k \text{ are real;}$$

$$\alpha=\frac{a}{q}+\frac{\theta}{q^2};\ (a,\ q)=1;\ 0<q\leqslant N^k;\ |\theta|\leqslant 1;$$

$$Q=\min\left(q,\ \frac{N^k}{q}\right)$$

Then we can choose a positive $\sigma=\sigma(k)$ depending only on k such that

$$|S|\leqslant c_2NQ^{-\sigma},$$

where c_2 is a constant, if

$$m \text{ is integral; } 0<m\leqslant Q^{2\sigma}.$$

4. Let $f(p)$, Q and σ be the same as in the result 3 and p run over the primes in the interval $0<p\leqslant N$.

Then for any ρ $(0<\rho\leqslant 1)$, the number of values of the fraction

$$\{f(p)\}$$

lying in the interval

$$0\leqslant\{f(p)\}\leqslant\rho$$

may be expressed by the formula

$$\rho\pi(N)+O(NQ^{-\sigma}\log N).$$

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REFERENCES

[1] I. M. Vinogradow, C. R. Acad. Sci. URSS, XV, № 6—7 (1937); I. M. Vinogradow, Recueil mathématique, 2 (44), № 2. [2] I. M. Vinogradow, C. R. Acad. Sci. URSS, XVI, № 3 (1937).

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MATHEMATICS

ON THE REPRESENTATION OF INTEGERS AS THE SUMS OF THE k^{th} POWERS OF PRIMES

By LOO-KENG HUA

(Communicated by I. M. Vinogradow, Member of the Academy, 1. X. 1937)

Let

$$a = \frac{1}{k}, \quad b = 18\,k^3 \log k, \quad m = \left[\frac{\log \frac{1}{2}\,b + \log(1-2a)}{\log\left(1+\frac{1}{k-1}\right)}\right],$$

$$c = \left[\frac{1}{2}\,b\,(k-2)\,(1-a)^{m+1}\right] + 1, \quad t = \operatorname{Max}(c,\ 4k)$$

and $c_1, \ldots$ are numbers depending only on k. Then

$$m = 3k \log k + k \log\log k + O(k).$$

Let N be a large integer and $P = \frac{1}{2}N^a$.

Theorem. Let $p^{\Theta} \mid\mid k$ and

$$K = \prod_{(p-1)/k} p^{\gamma}, \quad \gamma = \begin{cases} \Theta + 2 \text{ for } p = 2,\ 2/k \\ \Theta + 1 \text{ otherwise.} \end{cases}$$

Then

$$N = p_1^k + \ldots + p_s^k$$

is solvable for all large $N \equiv s \pmod K$, provided $k \geqslant 20$ and

$$s \geqq 2t + 2m + 7 \quad (\sim 6k \log k).$$

The proof of the theorem is depending on several results due to Vinogradow.

Let

$$T(\alpha,\ P) = \sum_{P<n<2P} e^{2\pi i n^k \alpha}, \quad T_i(\alpha) = T(\alpha,\ 2^{-i}P^{(1-a)^i}), \quad i = 0, \ldots, m+1,$$

$$Q(\alpha) = T_1(\alpha) \ \ldots \ T_m(\alpha)\, T_{m+1}^2(\alpha)$$

$$R(\alpha) = T_0(\alpha)\, Q(\alpha) = \sum_n r_{m+3}(n)\, e^{2\pi i n \alpha},$$

$$T_0^t(\alpha)\, R(\alpha) = \sum_n r_{t+m+3}(n)\, e^{2\pi i n \alpha}.$$

Then

$$c_1 P^{k-1-(k-2)(1-a)^{m+1}} \leqslant Q(0) \leqslant c_2 P^{k-1-(k-2)(1-a)^{m+1}}.$$

Lemma 1.

$$\sum_n \left[r_{t+m+3}(n) - \mathfrak{S}(n)\, c_3 n^{ta-1} R(0)\right]^2 = O\left(N^{2at-1-c_4} R^2(0)\right)$$

where $\mathfrak{S}(n)$ is the ordinally singular series for Waring problem.

The proof of lemma 1 depends essentially on a result due to Vinogradow (1) and

Lemma 2.

$$\int_0^1 |R(\alpha)|^2 d\alpha = \sum_n r_{m+3}^2(n) = O\left(P^{1+\varepsilon} Q(0)\right).$$

From lemma 1 we deduce

Lemma 3.

$$\sum_n r'^2_{t+m+3}(n) = O\left(N^{2ta-1} R^2(0)\right).$$

Further we put

$$T'(\alpha, P) = \sum_{P<p<2P} e^{2\pi i p^k \alpha}.$$

Similarly we define $T'_i(\alpha)$, $Q'(\alpha)$ and $R'(\alpha)$. Let

$$T_0'^{2t+1}(\alpha) R'^2(\alpha) = \sum_n r'_{2t+2m+7}(n)\, e^{2\pi i n \alpha}.$$

By Vinogradow's lemma (2) and lemma 3 we prove that if $s_0 = 2t + 2m + 7$, then we have

$$r'_{s_0}(n) = c_5 S(N) N^{(2t+1)a-1} R^2(0) L^{-s_0} + O\left(N^{(2t+1)a-1} R^2(0) L^{-s_0-\varepsilon}\right)$$

where $\varepsilon > 0$, $L = \log N$ and

$$S(N) = \sum_{q=1}^{\infty} W(q), \quad W(q) = q_1^{-s_0} \sum_{\substack{(a,q)=1 \\ 0 \leqslant a < q}} R_{a,q}^{s_0} e^{-\frac{2\pi i a N}{q}}$$

$$q_1 = \varphi(q), \quad R_{a,q} = \sum_{\substack{(x,q)=1 \\ 0 \leqslant x < q}} e^{\frac{2\pi i a x^k}{q}}.$$

Since $S(N) > 0$ for $N \equiv s \pmod K$, we have the theorem.

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REFERENCES

[1] Recueil Math., 1 (43), 175—188 (1936). [2] C. R. Acad. Sci. URSS, XVI, № 3 (1937).

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MATHEMATIK

ZUR LAPLACE-TRANSFORMATION. IX

Von V. S. IGNATOVSKIJ (W. IGNATOWSKY), korrespondierendem Mitglied der Akademie

Wir wollen hier die Resultate unserer Note V (1) und die entsprechende Bemerkung in der Note VIII (2) zusammenfassen und ergänzen.

Es sei*

$$f(z) = \int_0^\infty e^{-zt} F(t)\, dt, \tag{1}$$

und die hierzu, unter gewissen Bedingungen, gehörende Umkehrformel

$$F(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zt} f(z)\, dz. \tag{2}$$

Wie aus Note V hervorgeht, handelt es sich nicht um explizite gegebene reziproke Funktionen [d. h. solche die (1) und (2) zugleich genügen] sondern um gegebene Eigenschaften, und zwar solche, welche eine ganze Klasse reziproker Funktionen chararkterisieren. Es müssen dann augenscheinlich diese Eigenschaften zu einander reziprok sein, wie wir dies weiter unten ersehen werden.

Zu unserer Note V zurükkehrend, führen wir folgendes an: falls

$$F(t) = \frac{t^{\nu-1}}{\Gamma(\nu)} \{A_0 + B_0[\psi(\nu) - \lg t]\}; \quad t \to 0; \quad \nu > 0 \tag{3}$$

ist, wird für die Funktion $f(z)$**

$$f(z) = \frac{A_0 + B_0 \lg z}{z^\nu}; \quad |z| \to 0; \quad \nu > 0; \tag{4}$$

innerhalb der Konvergenzhalbebene H der Funktion $f(z)$ gelten. Dies folgt aus (1) und wird ähnlich bewiesen mit Hilfe von (20), Note VIII, wie dies bekanntlich für den Fall $B_0 = 0$ geschieht.

Wir müssen endlich auf die entsprechenden Sätze von sogenanntem Tauberschem Charakter hinweisen. In unserem Fall besagt dies: aus den Eigenschaften von $f(z)$ auf solche von $F(t)$ zu schliessen; z. B. gilt

* Als untere Grenze haben wir Null angenommen, was, ohne Einschränkung der Allgemeinheit, für das Folgende bequemer ist. Die notwendigen Änderungen bei einer unteren Grenze a (a ist endlich) sind aus der Note V ersichtlich.

** Statt (4) können wir auch schreiben $f(z) = \frac{A_0}{z^\nu} + \frac{B_0 \lg z}{z^\mu}$; $\nu > 0$, $\mu > 0$, mit der entsprechenden Änderung auch von (3).

bekanntlich, falls $f(z)$ die Eigenschaft (4) besitzt [bewiesen bei $B_0 = 0$ in (3) und (4)], dass dann $F(t)$ durch (3) charakterisiert wird*.

Hierbei müssen wir aber ausdrücklich hervorheben, dass erstens dieser Tatbestand ebenfalls auf Grund nur von (1) bewiesen wird [(2) wird dabei überhaupt nicht benützt] und zweitens wird von vornherein das Bestehen des dritten Integrals (18) in Note VIII vorausgesetzt**.

Diese Voraussetzung ist aber eine Annahme bezüglich einer Eigenschaft von $F(t)$, wärend wir über eine solche gerade auf Grund der Eigenschaften von $f(z)$ urteilen wollen.

Dieser Umstand veranlasste uns eben diese Frage in den Noten V und VIII noch einmal aufzunehmen und es ergab sich auch tatsächlich, dass das Bestehen des dritten Integrals (18), in Note VIII, hierbei eine wesentliche Rolle spielt.

Das am Schluss der Note V angeführte Beispiel nimmt, selbstverständlich unter Innehaltung der Bedingungen (5) und (4), Note V, eine, bei den in den Anwendungen vorkommenden Funktionen, plausible Eigenschaft in Anspruch, worauf die Existenz des dritten Integrals (18), in Note VIII, praktisch auch allgemein folgt.

Nun lässt sich dieses aber auch streng beweisen, denn tatsächlich ergibt sich, nun aber jetzt auf Grund von (2), dass falls für $f(z)$ die Eigenschaft (4) angenommen wird, es dann für $F(t)$ die Beziehung (3) folgt***. Hierbei fliesst dann aber die Existenz des obigen Integrals und weiter, auf Grund der Noten V und VIII, die Reprozität von $f(z)$ und $F(t)$****.Als nicht triviales Beispiel führen wir an:

$$\frac{\operatorname{arc\,sin\,h}\sqrt{z^2-1}}{\sqrt{z^2-1}} = \int_0^\infty e^{-zt} K_0(t)\,dt, \tag{5}$$

welches von Watson stammt*****, und wobei, erstens:

$$\left.\begin{aligned} &\frac{\lg 2z}{z} = f(z);\ |z| \to \infty, \\ &-\lg\frac{t}{2} - \gamma = K_0(t);\ t \to 0, \end{aligned}\right\} \tag{6}$$

($\gamma = 0.57721\ \ldots$ = Eulersche Konstante)

folgt, dass dieses mit (3) und (4) übereinstimmt und, zweitens, in $K_0(t)$ für $t \to 0$ übergeht******.

Allgemein bemerken wir, dass falls

$$|f(z)| \to 0;\ |z| \to \infty \tag{7}$$

in H ist, so haben wir dort

$$F(t) = 0;\ t < 0. \tag{8}$$

Ist in H

$$|f(z)\,z| \to 0;\ |z| \to \infty, \tag{9}$$

so folgt

$$F(t) = 0;\ t \leqslant 0 \tag{10}$$

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* Siehe Doetsch (3), S. 150, Satz II'.

** Siehe Doetsch (3), S. 145, Anmerkung 3.

*** Hierbei ist wieder (20) der Note VIII benutzt worden und auf (2) der Cauchysche Integralsatz angewandt, unter Beachtung, dass die Differenz zwischen $F(t)$ und (3), auf Grund der Beziehungen (10) und (12) des Textes, bei $t \to 0$ verschwindet.

**** Typisch hierfür ist das Buch von Bochner (4), welcher immer die Umkehrformel heranzieht und welcher auch teilweise die Laplace-Transformation behandelt. In seiner Nomenklatur entspricht der Fall $0 < \nu \leqslant 1$, resp. $0 < \mu \leqslant 1$, der Funktion $\mathfrak{F}_1$, und $1 < \nu$, resp. $1 < \mu$, der Funktion $\mathfrak{F}_0$.

***** Watson (5), S. 388.

****** Watson (5), S. 80.

und, allgemein, wenn in H

$$|f(z)\, z^{p+1}| \to 0; \quad |z| \to \infty \tag{11}$$

ist, so ergibt sich

$$\frac{d^p F(t)}{dt^p} = 0; \quad t \leqq 0. \tag{12}$$

Nun sei, entgegen der Beziehung (4) und (5), Note V,

$$f(z) = \frac{e^{-\alpha e^{i\delta} z^\beta}}{z^\nu} \tag{13}$$

mit reellem

$$\alpha > 0 \tag{14}$$

und

$$0 < \beta < 1. \tag{15}$$

Aus (13) folgt ($z = re^{i\varphi}$)

$$|f(z)| = \frac{e^{-\alpha r^\beta \cos(\delta + \varphi\beta)}}{r^\nu}. \tag{16}$$

Aus den obigen allgemeinen Beziehungen ersehen wir, dass bei Innehaltung der Bedingung

$$|\delta \pm \varphi\beta| \leqq \frac{\pi}{2}, \tag{17}$$

(wobei $|\varphi| \leqq \frac{\pi}{2}$ sein wird) o h n e das Gleichheitszeichen, oder bei $\delta = 0$, für das entsprechende $F(t)$ die Beziehung (10), resp. (12), gelten wird, und zwar bei einem beliebigen reellen ν.

Gilt in (17) das Gleichheitszeichen, für irgend ein φ, so wird (8) bei $\nu > 0$ und (10) bei $\nu > 1$ erfüllt.

Rechnen wir aber nun direkt mit (16), laut (2) und dem Integralsatz von Cauchy, so erhalten wir für das Bestehen von (10) die viel günstigere Bedingung:

$$\nu > 1 - \beta. \tag{18}$$

Wir nehmen nun $\beta = \frac{1}{2}$ an und erhalten unter vielem anderen folgende Relationen. Das aus (13) entsprechende $F(t)$ lautet:

$$F(t) = \frac{1}{\Gamma\left(\nu - \frac{1}{2}\right)} \int_0^t \frac{e^{-\frac{\alpha^2 e^{2i\delta}}{4y}} (t-y)^{\nu - \frac{3}{4}}}{\sqrt{\pi y}}\, dy; \quad \nu > \frac{1}{2}. \tag{19}$$

Speziell für $\delta = 0$ haben wir

$$\frac{\alpha}{2\Gamma(\nu)} \int_0^t \frac{e^{-\frac{\alpha^2}{4y}} (t-y)^{\nu-1}}{y^{\frac{3}{2}}}\, dy = \frac{1}{\Gamma\left(\nu - \frac{1}{2}\right)} \int_0^t \frac{e^{-\frac{\alpha^2}{4y}} (t-y)^{\nu-1}}{\sqrt{y}\sqrt{t-y}}\, dy; \quad \nu > \frac{1}{2}, \tag{20}$$

und bei $\nu = \frac{1}{2}$:

$$\frac{e^{-\frac{\alpha^2}{4t}}}{\sqrt{\pi t}} = \frac{\alpha}{2\pi} \int_0^t \frac{e^{-\frac{\alpha^2}{4y}}}{y^{\frac{3}{2}}\sqrt{t-y}}\, dy. \tag{21}$$

Ferner wird, wieder bei $\nu = \frac{1}{2}$:

$$F(t) = \frac{1}{\sqrt{\pi t}} e^{-\frac{\alpha^2 e^{2i\delta}}{4t}}; \qquad \begin{matrix} t \geqslant 0; & \delta < \frac{\pi}{4} \\ t > 0; & \delta = \frac{\pi}{4} \end{matrix} \tag{22}$$

mit

$$f(z) = \frac{e^{-\alpha\sqrt{z}\cdot e^{i\delta}}}{\sqrt{z}}. \tag{23}$$

Hieraus kommen wir bei $\delta = \pm\frac{\pi}{4}$, zu dem folgenden Paar reziproker Funktionen*:

$$f(z) = \frac{e^{-\frac{\alpha\sqrt{z}}{\sqrt{2}}}}{\sqrt{z}} \sin\frac{\alpha\sqrt{z}}{\sqrt{2}}; \quad F(t) = \frac{\sin\frac{\alpha^2}{4t}}{\sqrt{\pi t}}. \tag{24}$$

Nun ist $\frac{df(z)}{dz}$ eine Funktion von selbem Typus wie (24), weshalb auf Grund der Note V und (18) $\left(\beta = \frac{1}{2}\right)$ erhalten wir, dass $tF(t) = 0$ bei $t = 0$ sein wird. Dies ergibt sich auch tatsächlich aus (22). Anderseits ersehen wir, dass $tF(t)$, bei der Annäherung von t an Null, unendlich oft das Vorzeichen wechseln wird, entgegengesetzt als bei dem am Schluss der Note VIII angenommenen Beispiel. Dafür ist aber auch das Verhalten von $f(z)$ in (24) bei $|z| \to \infty$ ein vollständig verschiedenes von (4) und (5) der Note V. Das Integral (1) ist aber absolut konvergent und existiert deshalb das rechte Integral in (18) Note VIII**.

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ZITIERTE LITERATUR

[1] V. Ignatovskij, C. R. Acad. Sci. URSS, XIV, № 8, 475—478 (1937). [2] V. Ignatovskij, C. R. Acad. Sci. URSS, XV, № 5, 231—234 (1937). [3] G. Doetsch, Sätze vom Tauberschen Charakter..., Berl. Ber. d. Akad. d. Wiss. phys.-math. Klasse, X, 144—157 (1930). [4] S. Bochner, Vorl. ü. Fouriersche Integrale, S. 145 u. folg. (1932). [5] G. N. Watson, Theory of Bessel Funktion (1922). [6] G. Meyer, Vorl. ü. d. Theorie d. bestimmten Integrale (1871). [7] Vlad. Bernstein, Progrès récents de séries de Dirichlet (1933).

* Siehe Bochner ([4]), S. 57, Formel (13) und G. Meyer ([6]), S. 330.

** Siehe auch das Buch von V. Bernstein ([7]), welches in der Note III, S. 294 fast vollständig den Fall $\nu > 1$ behandelt.

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THEORY OF ELASTICITY

THE PROBLEM OF CONTACT OF AN ELASTIC INFINITE HALF-PLANE WITH AN ABSOLUTELY RIGID ROUGH FOUNDATION

By B. M. ABRAMOV (ABRAMOFF)

(Communicated by S. A. Chaplygin, Member of the Academy, 22. VII. 1937)

This problem, presented in a more general form and described as the foundamental mixed problem of the theory of elasticity for a half-plane, has been solved by N. I. Muschelišvili (1). The same problem is solved in this paper by another method.

Let an elastic half-plane occupy the lower half of the plane of the coordinates x, y, bounded by the axis x. The boundary conditions (the notation being after N. I. Muschelišvili) will be as follows:

$$u = g_1 + \text{const}, \quad v = g_2 + \text{const} \text{ on the segment } AB \text{ of the axis } x; \quad (1)$$

$$P = h_1, \qquad T = h_2 \qquad \text{on the axis } x \text{ outside } AB, \quad (2)$$

$$\int_{AB} T\,dx = X, \qquad \int_{AB} P\,dx = -Y = K, \quad (3)$$

where u, v are the components of displacement, $P = -Y_y$, normal stress, $T = X_y$, shearing stress, g_1, g_2, h_1, h_2, the given functions, (X, Y), the given resultant vector of tractions acting on AB. At infinity stresses must vanish. The problem is reduced (2) to finding two analytic functions $\varphi(z)$, $\psi(z)$ of the complex variable $z = x + iy$, regular in the lower half-plane and satisfying the boundary conditions:

$$\frac{\partial U}{\partial x} + i\frac{\partial U}{\partial y} = \varphi(x) + x\overline{\varphi'(x)} + \overline{\psi(x)} = f_1 + if_2 = -i\int_{-\infty}^{x}(T - iP)\,dx \quad (4)$$

outside $AB\,(|x| > l)$;

$$2\mu(u + iv) = \varkappa\varphi(x) - x\overline{\varphi'(x)} - \overline{\psi(x)} = 2\mu(g_1 + ig_2) \text{ on } AB\,(|x| < l). \quad (5)$$

Here U is Airy's function, $\varkappa = \dfrac{\lambda + 3\mu}{\lambda + \mu} = 3 - 4\nu$ where ν is Poisson's ratio and λ, μ are Lamé's elastic constants.

Let

$$z = l\frac{1-\zeta}{1+\zeta} \text{ whence } \zeta = \frac{l-z}{l+z} = \xi + i\eta. \quad (6)$$

The lower half-plane z will be then mapped on the upper half-plane ζ, and the segment AB on the positive part of the axis ξ. The point

$\zeta = \infty$ of the plane ζ will correspond to the point $A\,(x = -l)$, while the origin of the coordinates of the plane ζ will correspond to the point $B\,(x = l)$.

Here we introduce the following notation:

$$\varphi(z) = \varphi\Big(l\,\frac{1-\zeta}{1+\zeta}\Big) = \varphi_1(\zeta) = \varphi_1(re^{i\theta}), \tag{7}$$

$$z\varphi'(z) + \psi(z) = \tau(z) = \tau\Big(l\,\frac{1-\zeta}{1+\zeta}\Big) = \tau_1(\zeta) = \tau_1(re^{i\theta}). \tag{8}$$

As we have $\bar{z} = z$ on the real axis x the boundary conditions will be as follows:

$$\left.\begin{aligned} \varphi_1(re^{i\theta}) + \overline{\tau_1(re^{i\theta})} &= F(r) \text{ if } \theta = \pi; \\ \varkappa\varphi_1(re^{i\theta}) - \overline{\tau_1(re^{i\theta})} &= G(r) \text{ if } \theta = 0, \end{aligned}\right\} \tag{9}$$

where

$$\left.\begin{aligned} F(r) &= f_1\Big(l\,\frac{1+r}{1-r}\Big) + if_2\Big(l\,\frac{1+r}{1-r}\Big); \\ G(r) &= g_1\Big(l\,\frac{1-r}{1+r}\Big) + ig_2\Big(l\,\frac{1-r}{1+r}\Big). \end{aligned}\right\} \tag{10}$$

Let us assume that the functions $\varphi_1(\zeta)$ and $\tau_1(\zeta)$ are presented by Mellin's integrals (the real constant σ being properly chosen):

$$\left.\begin{aligned} \varphi_1(\zeta) &= \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} M(s)\,\zeta^{-s}\,ds = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} M(s)\,e^{-i\theta s}r^{-s}\,ds; \\ \tau_1(\zeta) &= \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} N(s)\,\zeta^{-s}\,ds = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} N(s)\,e^{-i\theta s}r^{-s}\,ds. \end{aligned}\right\} \tag{11}$$

Then

$$\overline{\tau_1(\zeta)} = \frac{1}{2\pi(-i)}\int_{\sigma-i\infty}^{\sigma+i\infty} \overline{N}(s)\,\zeta^{-s}\,ds = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \overline{N}(s)e^{i\theta s}r^{-s}\,ds. \tag{12}$$

Here $\overline{N}(s)$ represents into what is converted $N(s)$ when $-i$ is substituted for i, and then s for $\bar{s}$, e. g., if

$$N(s) = \sum a_k s^k \quad \text{then} \quad \overline{N}(s) = \sum \bar{a}_k s^k. \tag{13}$$

The boundary conditions can be expressed as follows:

$$\left.\begin{aligned} \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} [M(s)\,e^{-i\pi s} + \overline{N}(s)\,e^{i\pi s}]\,r^{-s}\,ds &= F(r), \\ \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} [\varkappa M(s) - \overline{N}(s)]\,r^{-s}\,ds &= G(r). \end{aligned}\right\} \tag{14}$$

If certain conditions are satisfied*, from the representation of the function $H(r)$ as Mellin's integral:

$$\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} h(s)\,r^{-s}\,ds = H(r), \tag{15}$$

we get the reciprocal transformation

$$h(s) = \int_0^\infty r^{s-1}H(r)\,dr \tag{16}$$

within a certain interval $\sigma_0 < \sigma = R\{s\} < \sigma_1$.

* Sufficient conditions see e. g. in [3].

Assuming the necessary conditions to have been satisfied and applying the formula (16) to (14), we shall get:

$$\left.\begin{aligned} M(s)\,e^{-i\pi s} + \overline{N}(s)\,e^{i\pi s} &= \int_0^\infty F(r)\,r^{s-1}dr = f(s), \\ \varkappa M(s) - \overline{N}(s) &= \int_0^\infty G(r)\,r^{s-1}dr = g(s). \end{aligned}\right\} \tag{17}$$

Consequently,

$$\left.\begin{aligned} M(s) &= \frac{f(s)}{e^{-i\pi s} + \varkappa e^{i\pi s}} + \frac{g(s)\,e^{i\pi s}}{e^{-i\pi s} + \varkappa e^{i\pi s}}, \\ \overline{N}(s) &= \frac{\varkappa f(s)}{e^{-i\pi s} + \varkappa e^{i\pi s}} - \frac{g(s)\,e^{-i\pi s}}{e^{-i\pi s} + \varkappa e^{i\pi s}}; \end{aligned}\right\} \tag{18}$$

whence it follows that

$$N(s) = -\frac{\varkappa \bar{f}(s)}{e^{i\pi s} + \varkappa e^{-i\pi s}} - \frac{\bar{g}(s)\,e^{i\pi s}}{e^{i\pi s} + \varkappa e^{-i\pi s}}. \tag{19}$$

Therefore

$$\left.\begin{aligned} \varphi_1(\zeta) &= \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{f(s) + g(s)\,e^{i\pi s}}{e^{-i\pi s} + \varkappa e^{i\pi s}}\,\zeta^{-s}\,ds, \\ \tau_1(\zeta) &= \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{\varkappa \bar{f}(s) - \bar{g}(s)\,e^{i\pi s}}{e^{i\pi s} + \varkappa e^{-i\pi s}}\,\zeta^{-s}\,ds. \end{aligned}\right\} \tag{20}$$

As an example we shall consider the case of the pressure of a foundation with a rectilinear base under a symmetrical action of the force (4). Here

$$g_1 = 0, \quad g_2 = 0, \tag{21}$$

$$f_1 = \begin{cases} 0 & \text{if } x < -l, \\ Y = -K & \text{if } x > l, \end{cases} \qquad f_2 = 0, \tag{22}$$

$$F(r) = \begin{cases} 0 & \text{if } r > 1, \\ Y = -K & \text{if } 0 < r < 1, \end{cases} \qquad G(r) = 0 \tag{23}$$

from which we get:

$$f(s) = \int_0^\infty F(r)\,r^{s-1}\,dz = \int_0^1 -Kr^{s-1}\,dr = -\frac{K}{s} \text{ if } \sigma = R\{s\} > 0,\ g(s) = 0, \tag{24}$$

$$\bar{f}(s) = -\frac{K}{s} = f(s), \quad \bar{g}(s) = 0. \tag{25}$$

Using (20), we will thus obtain:

$$\left.\begin{aligned} \varphi_1(\zeta) &= \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{-K\zeta^{-s}}{s\,(e^{-i\pi s} + \varkappa e^{i\pi s})}\,ds = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{-Ke^{-i\pi s}\,\zeta^{-s}}{s\,(e^{-2i\pi s} + \varkappa)}\,ds; \\ \tau_1(\zeta) &= \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{-K\varkappa\zeta^{-s}}{s\,(e^{i\pi s} + \varkappa e^{-i\pi s})}\,ds = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{-K\zeta^{-s}}{s\,(e^{-i\pi s} + \frac{1}{\varkappa}e^{i\pi s})}\,ds. \end{aligned}\right\} \tag{26}$$

It is to be noted that $\tau_1(\zeta)$ is obtained from $\varphi_1(\zeta)$ by the substitution of $\frac{1}{\varkappa}$ for $\varkappa$.

Let the straight line $s = \sigma > 0$ in the complex plane s be closed by a semi-circle of a large radius drawn, e. g., to the right of the straight line $s = \sigma$. To the right of this straight line we will have only the following simple poles of the integrand for $\varphi_1(\zeta)$:

$$s_n = i\frac{\ln \varkappa}{2\pi} + \frac{1}{2} + n\left(n = p, p+1, p+2, \ldots, \text{if } p - \frac{1}{2} < \sigma < p + \frac{1}{2}\right), \quad (27)$$

with residues

$$\mathcal{E}(s_n) = \left| -\frac{Ke^{-i\pi s}\,\zeta^{-s}}{s\,\frac{d}{ds}(e^{-2i\pi s} + \varkappa)} \right|_{s=s_n} = (-1)^n \frac{K}{2\pi\sqrt{\varkappa}} \frac{\zeta^{-s_n}}{s_n}. \quad (28)$$

Applying now Cauchy's theorem of residues, we shall get:

$$\varphi_1(\zeta) = -\sum_{n=p}^{\infty} \mathcal{E}(s_n) = -\sum_{n=p}^{\infty} (-1)^{n+1} \frac{K}{2\pi\sqrt{\varkappa}} \frac{\zeta^{-s_n}}{s_n} \quad (p = 0, 1, 2, \ldots), \quad (29)$$

according to that of the intervals $0 < \sigma < \frac{1}{2}$, $\frac{1}{2} < \sigma < \frac{3}{2}$, ..., $p - \frac{1}{2} < \sigma < p + \frac{1}{2}$ within which we shall have taken σ.

In order to make the summation we differentiate

$$\frac{d\varphi_1(\zeta)}{d\zeta} = \sum_{n=p}^{\infty} (-1)^n \frac{K}{2\pi\sqrt{\varkappa}} \zeta^{-s_n - 1} =$$

$$= (-1)^p \frac{K}{2\pi\sqrt{\varkappa}} \zeta^{-i\frac{\ln \varkappa}{2\pi} - \frac{3}{2} - p}\left(1 - \frac{1}{\zeta} + \frac{1}{\zeta^2} - \ldots\right) =$$

$$= (-1)^p \frac{K}{2\pi\sqrt{\varkappa}} \zeta^{-i\frac{\ln \varkappa}{2\pi} - \frac{1}{2} - p} \cdot \frac{1}{1+\zeta}. \quad (30)$$

The series is, of course, convergent if $|\zeta| > 1$ but the expression resulting from the summation gives $\frac{d\varphi_1(\zeta)}{d\zeta}$ at any $\zeta \neq -1$, in virtue of the possibility of an analytic continuation. Therefore,

$$\varphi_1(\zeta) = (-1)^p \frac{K}{2\pi\sqrt{\varkappa}} \int_0^{\zeta} \frac{\zeta^{-i\frac{\ln \varkappa}{2\pi} - \frac{1}{2} - p}}{1+\zeta}\, d\zeta + c, \quad (31)$$

$$\varphi(z) = (-1)^p \frac{K}{2\pi\sqrt{\varkappa}} \int_0^{\frac{l-z}{l+z}} \frac{\zeta^{-i\frac{\ln \varkappa}{2\pi} - \frac{1}{2} - p}}{1+\zeta}\, d\zeta + c. \quad (32)$$

Substituting $\frac{1}{\varkappa}$ for $\varkappa$, we get, in virtue of the above remark,

$$\tau(z) = z\varphi'(z) + \psi(z) = (-1)^p \frac{K\sqrt{\varkappa}}{2\pi} \int_0^{\frac{l-z}{l+z}} \frac{\zeta^{i\frac{\ln \varkappa}{2\pi} - \frac{1}{2} - p}}{1+\zeta}\, d\zeta + c. \quad (33)$$

The formula for $\varphi(z)$ shows that if $z \to \infty$ $(\zeta \to -1)$ $\varphi(z)$ behaves as $\ln z$ (whence it follows that $\varphi'(z)$ behaves as $\frac{1}{z}$). The same refers to $\tau(z)$, so that $\psi(z) = \tau(z) - z\varphi'(z)$ also behaves as $\ln z$ if $z \to \infty$ whence it follows that the stresses at infinity vanish.

The formula for the stresses acting at the line of contact with the foundation is derived below. As $\frac{l-x}{l+x} = \left|\frac{l-x}{l+x}\right|$ we have at $|x| < l$:

$$\frac{\partial U}{\partial x} + i\frac{\partial U}{\partial y} = \varphi(z) + \overline{\tau(z)} = (-1)^p \frac{K}{2\pi\sqrt{\bar{x}}} \int_0^{\frac{l-x}{l+x}} \frac{\zeta^{-i\frac{\ln x}{2\pi}-\frac{1}{2}-p}}{1+\zeta}\, d\zeta + c + \cdot$$

$$+ (-1)^p \frac{K\sqrt{\bar{x}}}{2\pi} \int_0^{\frac{l-x}{l+x}} \frac{\zeta^{-i\frac{\ln x}{2\pi}-\frac{1}{2}-p}}{1+\zeta}\, d\zeta + \bar{c} =$$

$$= (-1)^p \frac{K(1+x)}{2\pi\sqrt{\bar{x}}} \int_0^{\frac{l-x}{l+x}} \frac{\zeta^{-i\frac{\ln x}{2\pi}-\frac{1}{2}-p}}{1+\zeta}\, d\zeta + c'. \qquad (34)$$

Differentiation with respect to x results in the following:

$$\frac{\partial^2 U}{\partial x^2} + i\frac{\partial^2 U}{\partial x \partial y} = Y_y - iX_y =$$

$$= (-1)^p \frac{K(1+x)}{2\pi\sqrt{\bar{x}}} e^{-i\frac{\ln x}{2\pi}\ln\frac{l-x}{l+x}} \cdot \left(\frac{l-x}{l+x}\right)^{-\frac{1}{2}-p} \cdot \frac{-1}{l+x} \qquad (35)$$

and hence

$$Y_y = (-1)^{p+1} \frac{K(1+x)}{2\pi\sqrt{\bar{x}}} \cos\left(\frac{\ln x}{2\pi}\ln\frac{l-x}{l+x}\right) \cdot \frac{1}{\sqrt{l^2-x^2}} \left(\frac{l-x}{l+x}\right)^{-p}, \qquad (36)$$

$$X_y = (-1)^{p+1} \frac{K(1+x)}{2\pi\sqrt{\bar{x}}} \sin\left(\frac{\ln x}{2\pi}\ln\frac{l-x}{l+x}\right) \cdot \frac{1}{\sqrt{l^2-x^2}} \cdot \left(\frac{l-x}{l+x}\right)^{-p} \qquad (37)$$

$$(p = 0, 1, 2, \ldots).$$

It may be easily seen that negative whole values of p also give solutions of the problem. The same refers also to a combination of all these solutions with properly chosen coefficients. Such a multiplicity of solutions is to be accounted for by the fact that the boundary conditions (1) and (2), etc., are expressed in the same way regardless of whether any concentrated forces, moments and more complicated singularities are applied at points A and B (foundation corners) or not.

Only one solution corresponding to $p = 0$ satisfies the conditions of the uniqueness theorem* proved by N. I. Muschelišvili [(1), pages 321, 322, 330]. This method provides only a part of additional solutions, which is due to the fact that the representation of the functions $\varphi_1(\zeta)$ and $\tau_1(\zeta)$ in the form of Mellin's integrals is possible only under certain conditions of behaviour of these functions at points $\zeta = 0$ and $\zeta = \infty$. The same conditions also determine the permissible values of σ; e. g., it is easy to establish that, if regularity of functions is required at these points, we should take $0 < \sigma < 1$. The correctness of this solution is readily proved by direct verification.

* These conditions consist in vanishing of all the stresses and of the magnitude $y\frac{\partial}{\partial y}(X_x + Y_y)$ at $|z| \to \infty$. The proof is based on the application of Green's formula for the transformation of a double integral into a simple one and is not directly applicable to this case because of the singularities at different points of the contour. Cutting out the neighbourhood of these points and passing on to the limit, we get the necessary generalization.

The case $p = 0$, which satisfies the conditions of the uniqueness theorem, gives us

$$\left.\begin{aligned} Y_y &= -\frac{K}{\pi}\frac{1}{\sqrt{l^2-x^2}}\frac{1+\varkappa}{2\sqrt{\varkappa}}\cos\left(\frac{\ln\varkappa}{2\pi}\ln\frac{l-x}{l+x}\right), \\ X_y &= -\frac{K}{\pi}\frac{1}{\sqrt{l^2-x^2}}\frac{1+\varkappa}{2\sqrt{\varkappa}}\sin\left(\frac{\ln\varkappa}{2\pi}\ln\frac{l-x}{l+x}\right). \end{aligned}\right\} \qquad (38)$$

If $\varkappa = 1$ (i. e. Poisson's ratio $\nu = 0.5$), the first formula agrees with the well-known formula derived by Sadowsky [5] for the case of absence of forces due to friction:

$$Y_y = -\frac{K}{\pi}\frac{1}{\sqrt{l^2-x^2}}, \quad X_y = 0. \qquad (39)$$

In this particular case of $\nu = 0.5$, both the forces due to friction and slipping are absent.

The formula (38) shows that at any $\varkappa \neq 1$ (i. e., when $\nu < 0.5$) the stress Y_y (as well as X_y) changes its sign an infinite number of times close to the corners of the foundation. When approaching the corners of the foundation, the stress Y_y changes for the first time its sign from a negative to a positive, if

$$x = \pm l \cdot \operatorname{th}\frac{\pi^2}{2\ln\varkappa}.$$

As $0 \leqslant \nu \leqslant 0.5$ and therefore $1 \leqslant \varkappa \leqslant 3$ it follows that the least value of x is obtained when $\varkappa = 3$, which gives

$$x = \pm l \cdot \operatorname{th}\frac{9.8696}{2 \cdot 1.0986} = \pm 0.9997\, l.$$

But it is obvious that regions with permanent deformation will be reduced close to the corners of the foundation and therefore non-compliance with the self-understood requirement $Y_y < 0$ (under the foundation) close to the corners is of no importance whatsoever.

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REFERENCES

[1] N. Muschelišvili, C. R. Acad. Sci. URSS, III (VIII), № 2 (62) (1935). Н. И. Мусхелишвили, Некоторые основные задачи теории упругости, 2-е изд. (1935). [3] R. Courant, D. Hilbert, Methoden der mathematischen Physik, Bd. 1, S. 90—93. [4] В. А. Флорин, Сб. Гидростройпроекта, Гидротехн. вып. 1, 21—34 (1936). [5] M. Sadowsky, ZS. f. angew. Math. u. Mech., 8, 107—121 (1928).

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«ANOMALE» ANTISTOKESSCHE FLUORESZENZ

Von F. DUSCHINSKY

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Bekanntlich zeigen manche organische Farbstoffe in Lösung oder im Dampfzustand in übergewöhnlichem Ausmass die Erscheinung der antistokesschen Fluoreszenz. Nach N. Prileshajewa (1) lässt sich z. B. Anilindampf mit merklicher Intensität noch in einem Spektralgebiet zur Fluoreszenz anregen, das gegenüber deren kurzwelligen Grenze um mehr als 1 Volt nach langen Wellen verschoben ist. Wenn diese Angabe auch nur halbquantitative Bedeutung hat, erkennt man doch, dass Fluoreszenz mit einer derartigen antistokesschen Verschiebung bei zweiatomigen Molekülen bei 200° C keinesfalls mehr beobachtbar sein kann. Man kann leicht ausrechnen, dass ihre Intensität um einen Faktor 10^{-11} schwächer sein müsste als bei stokesscher Erregung. Warum aber bei mehratomigen Molekülen eine derartige antistokessche Fluoreszenz möglich ist, ist eine bisher noch nicht völlig aufgeklärte Frage.

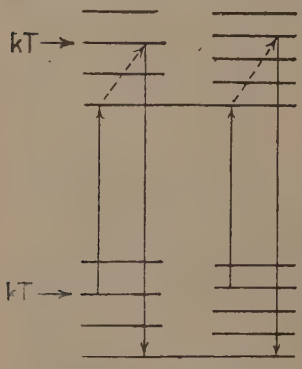
Ohne Zweifel hängt die Erscheinung mit der grossen Zahl der inneren Freiheitsgrade des komplizierten Moleküls zusammen und die Behauptung von Prileshajewa, dass beim Anilin die Energie der antistokesschen Fluoreszenz thermisch nicht gedeckt werden kann, beruhte auf einem Irrtum, der später von Terenin (2) richtiggestellt wurde. Energetisch besteht also keine Schwierigkeit. Die Frage ist nur, wie die über alle Freiheitsgrade verteilte Wärmeenergie sich bei der Fluoreszenzemission in e i n e m Quant konzentrieren kann. Die von Terenin vertretene Auffassung, dass man es hier mit einer zeitweiligen Konzentration der thermischen Energie in einen Teil des Moleküls, aus dem die Emission erfolgt, zu tun habe, stösst auf grosse Schwierigkeiten. Solche Zustände anomaler Energieverteilung mit einer Verweilzeit, vergleichbar der mittleren Lebensdauer des angeregten Zustandes, sind thermodynamisch äusserst unwahrscheinlich; als thermische Schwankungserscheinung können sie praktisch nicht auftreten. Man könnte an eine gesetzmässige Pendelung der Energie innerhalb des Moleküls denken, etwa infolge der Anharmonizität der Kernbindungskräfte, die einen Übergang der Schwingungsenergie aus einer Normalschwingung in eine andere ermöglichen könnte; aber selbst wenn dadurch im isolierten Molekül eine längerlebige anomale Energieverteilung zustande kommen könnte, würde sie durch Stösse mit den Molekülen der Umgebung sofort wieder zerstört werden, wofür ja die Unabhängigkeit des Fluoreszenzspektrums von der Wellenlänge des anregenden Lichtes den experimentellen Beweis liefert. Eine Konzentration der thermischen Energie auf einzelne

Freiheitsgrade des Moleküls kommt also zur Erklärung des Effektes kaum in Frage. Eine derartige künstliche Annahme ist aber auch gar nicht notwendig. Die Quantentheorie der Molekülspektren liefert die Erklärung ganz von selbst und auf einfachste Weise. Die «anomale» antistokessche Fluoreszenz ist danach—was hier kurz gezeigt werden soll—eine unter gewissen Bedingungen beim mehratomigen Molekül durchaus zu erwartende Erscheinung.

Beim zweiatomigen Molekül erfolgt gleichzeitig mit dem Elektronensprung in der Regel auch ein Sprung der Kernschwingungs- und der Rotationsquantenzahl, wobei bekanntlich die g e s a m t e Energie, die hierbei frei wird, in e i n e m Quant ausgestrahlt wird. Beim mehratomigen Molekül werden sich im allgemeinen auch noch die übrigen Schwingungsfreiheitsgrade an dem Elementarakt beteiligen; welche von ihnen und in welchem Masse, lässt sich nur in jedem einzelnen Fall mit Hilfe des Franck-Condon-Prinzipes entscheiden. Zur Ausstrahlung gelangt also, wenn man die Anharmonizität vernachlässigt, eine Frequenz

$$\nu = \frac{1}{h}(E_{el} + \Delta E_{rot}) + \left(v_1' + \frac{1}{2}\right)\omega_1' + \left(v_2' + \frac{1}{2}\right)\omega_2' + \ldots - \\ - \left(v_1'' + \frac{1}{2}\right)\omega_1'' - \left(v_2'' + \frac{1}{2}\right)\omega_2'' - \ldots \qquad (1)$$

(Die Bezeichnungen verstehen sich wohl von selbst.) Wir betrachten nun als einfachstes Beispiel, an dem jedoch alles Wesentliche zu ersehen ist, ein Molekül mit nur 2 Normalschwingungen; dass es in Wirklichkeit ein solches Molekül nicht gibt, tut nichts zur Sache. Ist die Temperatur hinreichend hoch und sind die Eigenfrequenzen hinreichend klein (eine Einschränkung, die die Betrachtung vereinfacht, aber keine prinzipielle Bedeutung hat), so kommt im Temperaturgleichgewicht auf jede der beiden Normalschwingungen eine mittlere Energie von annähernd kT (Boltzmannkonstante $\times$ absolute Temperatur) und die langwelligste, noch mit merklicher Intensität mögliche Absorption wird ihrem gleichzeitigen Übergang $(kT)'' \to 0'$ (Figur) entsprechen; vorausgesetzt natürlich, dass das Franck-Condon-Prinzip diesen zulässt. Schematisch können wir diesen Übergang mit $\uparrow \binom{0}{kT}\binom{0}{kT}$ bezeichnen wobei wir einfach kT anstelle der dieser Energie enstprechenden Schwingungsquantenzahl schreiben. Wenn wir von der Rotation absehen—und eine nachträgliche Überlegung, die man leicht anstellen kann, rechtfertigt dies—ergibt sich nach (1) als Absorptionsfrequenz $\nu_{abs} = \frac{E_{el}}{h} - 2kT$. Bevor es noch zur Reemission kommt wird sich im angeregten Zustand Temperaturgleichgewicht herstellen, d. h. es werden beide Normalschwingungen auf Kosten der thermischen Energie der Umgebung im Mittel wieder



Die einander entsprechenden Übergänge im rechten und linken Teil der Fig. erfolgen gleichzeitig, sowohl für Absorption wie für Emission. Absorbiert, bezw. emittiert wird dabei die Summe der Frequenzen, die beide Teile als getrennte Systeme liefern würden, vermindert um die Frequenz des reinen Elektronensprunges (0-0-Übergang). Die gestrichelten Übergänge erfolgen durch Stösse.

eine Schwingungsenergie von je kT annehmen. Von den entsprechenden Schwingungsniveaus kann nun (wieder, falls dies mit dem Franck-Condon-Prinzip verträglich ist) mit merklicher Intensität die dem Übergang $\downarrow\binom{kT\ kT}{0\ \ 0}$ (Figur!) entsprechende Frequenz $\nu_{em}=\frac{E_d}{h}+2kT$ emittiert werden. Wir haben antistokessche Fluoreszenz mit einem Energiegewinn von $4kT$!

Man sieht, dass das ganze Problem auf die Anwendung des Franck-Condon-Prinzipes auf mehratomige Moleküle hinausläuft. Zwei allgemeine Bemerkungen lassen sich hierzu noch machen:

1. Ändern sich beim Elektronensprung die Eigenfrequenzen des Moleküls wenig, so werden der Energie kT im oberen wie im unteren Zustand je gleiche Schwingungsquantenzahlen entsprechen. Bezeichnen wir schematisch die Schwingungsquantenkonfiguration im unteren Zustand mit a'', im oberen mit b', so haben wir es bei Absoprtion mit einem Übergang $a''\rightarrow b'$ zu tun; der Emission hingegen entspricht in dem von uns betrachteten Fall ein Übergang $b''\prec a'$. Wir haben spiegelbildlich gleiche Konfigurationen für Absorption und Emission! Ist der eine Übergang erlaubt, so wird es meistens auch der andere sein. Zeigen Absorptions- und Emissionsspektrum «Spiegelkorrespondenz», so werden die beiden betrachteten Übergänge (relativ) g l e i c h e Wahrscheinlichkeiten haben, denn gerade dies ist eine für das Zustandekommen der Spiegelkorrespondenz notwendige Bedingung [3].

2. Der Hauptbeitrag zur antistokesschen Fluoreszenz wird von den totalsymmetrischen Normalschwingungen des Moleküls geliefert werden, denn alle anderen bevorzugen mehr oder weniger Übergänge mit $\Delta v=0$ [4]: anomale antistokessche Fluoreszenz wird also nur an Molekülen zu beobachten sein, die eine hinreichende Anzahl totalsymmetrischer Schwingungen besitzen; das Molekül muss also hinreichend komplex sein und einen nicht zu hohen Symmetriegrad aufweisen. Dies sind notwendige, aber nicht hinreichende Bedingungen.

Dass auch beliebig grosse antistokessche Verschiebungen mit dem 2. Hauptsatz der Thermodynamik nicht im Widerspruch stehen, wie es den Anschein haben könnte, liesse sich durch Übertragung einer von P. Pringsheim [5] für andere Fälle angestellten Überlegung zeigen.

Die dargestellte Auffassung über den Mechanismus der antistokesschen Fluoreszenz ist experimentell prüfbar; hierauf, sowie auf Einzelheiten soll jedoch an anderer Stelle eingegangen werden. Hier sei nur noch auf eine Erscheinung hingewiesen, die in engem Zusammenhang mit der von uns diskutierten Frage steht. Es handelt sich um das Vorschreiten der Absorptionsgrenze aus dem Ultraviolett nach langen Wellen, das man bei Temperaturerhöhung an durchsichtigen Körpern und Flüssigkeiten beobachten kann. Für zweiatomige Moleküle wird man der thermischen Anregung der Schwingung auf kT entsprechend ein Vorrücken der Absorptionsgrenze gerade um k pro Grad erwarten. Versuche an mehratomigen Substanzen ergeben dagegen ein bedeutend rascheres Vorrücken; z. B. ergibt sich aus Messungen von Weizel und Wolff [6] über die Temperaturabhängigkeit der Lichtabsorption verschiedener (ungefärbter) Gläser zwischen 30 und 500 C in der Gegend um 3 200 A ein Vorrücken des Gebietes gleicher Absorption um 9—14 cm^{-1} pro Grad. In cm^{-1} ° C ausgedrückt ist $k=0.70$. Die Absorptionsgrenze rückt also um 13—20 k pro Grad vor. An manchen Überfanggläsern für Dunkelkammerbeleuchtung kann der Effekt so grob werden, dass einige Zeit nach dem Einschalten, wenn sich das Filterglas hinreichend erwärmt hat, die Lampe merklich «dunkler brennt» [7]. Die Deutung dieser Erscheinungen ergibt sich aus dem vorhergehenden: Es erfolgt zusammen

mit dem Elektronensprung eine Änderung der Schwingungsquantenzahlen mehrerer Normalschwingungen gleichzeitig.

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ZITIERTE LITERATUR

[1] N. Prileshajewa, Acta Physicochimica URSS, **1**, 785 (1935). [2] A. Terenin, Acta Physica Pol., **5** (Kongressnummer), 253 (1936). [3] W. Lewschin, Acta Physicochimica URSS, **6**, 213 (1937). [4] G. Herzberg u. E. Teller, ZS. f. phys. Chem., **21** (B), 410 (1933). [5] P. Pringsheim, ZS. f. Physik, **57**, 739 (1929) [6] W. Weizel u. H. W. Wolff, ZS. f. techn. Phys., **11**, 358 (1930). [7] K. Weber ZS. f. wiss. Phot., **35**, 193 (1936).

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PHYSICS

LUMINESCENT-PHOTOGRAPHIC METHOD OF MEASURING THE ENERGY DISTRIBUTION IN THE ULTRA-VIOLET

By L. N. ANANJEVA and A. A. SHISHLOVSKY

(Communicated by S. I. Wawilow, Member of the Academy, 13. VIII. 1937)

There has hitherto been no satisfactory method of measuring the distribution of energy in the ultra-violet region of the spectrum. The chief difficulty in working out a method is connected with the absence of a suitable standard source of light with a known distribution of energy in the spectrum. Tungsten lamps with a quartz window, or the crater of an arc lamp, make it possible at best to measure the spectrum with more or less reliability only as far as 2500 Å. But for modern technical purposes, for physics, astrophysics, biology and medicine, it is often extremely important to know the distribution of energy in more remote parts of the ultra-violet spectrum of various sources of light, and this must moreover by obtainable rapidly without any great difficulty by ordinary laboratory means.

In 1927, S. I. Wawilow (1) and later W. Fabrikant (2) established experimentally that the emission of light from fluorescent solutions in the short-wave region is directly proportional to the wave length of the excitant light:

$$\frac{\rho_1}{\rho_2} = \frac{\lambda_1}{\lambda_2}.$$

Thus they proved that the photo-chemical law of the elementary processes of Einstein are also applicable to the processes of photoluminescence. In addition, it is known that the spectrum of the fluorescent solutions of many substances does not depend on the wave length of the excitant light. Along with the above-mentioned law of Wawilow, this made it possible to elaborate a new method of visual luminescent spectrophotometry. The main advantage of the luminescent method is that it does not demand a known source of ultra-violet light as a standard, by means of which the apparatus used is usually graduated, such as a photoelement in photographic methods of measurement. Measurement are made directly according to the intensity of the fluorescence, which gives directly the relative distribution of energy in the spectrum under examination:

$$\frac{E_{\lambda_0}}{E_{\lambda_n}} = \frac{I_{\lambda_0}}{I_{\lambda_n}} \cdot \frac{\lambda_n}{\lambda_0}$$

where $I = \rho E$ and E is the energy absorbed.

The only shortcoming of the visual luminescent method is the amount of work it entails and the troublesome measurements, especially measurements of faint lines or bands, in which it is necessary to resort to the so-called photometric method of quenching, which also requires a certain knack from the observer. It is, therefore, desirable to work out a photographic method of luminescent spectrophotometry.

It is known that in order to make photographic material sensitive to extreme ultra-violet rays in the region of 2400—2000 Å, the plates are washed with machine oil or with some other fluorescent solution. In 1931, Harrison and Leighton ([3]) even tried to work out a method by this means for heterochrome photometry, in particular washing the plates with a gelatine solution of eskulin. But the experimental results they obtained from the examination of the light emission of fluorescence according to the wave length of the exciting light were contradictory to the figures of Wawilow and Fabrikant, owing to some mistakes in principle of the measurements, which was pointed out in 1932 by Fabrikant ([2]). In order to obtain a satisfactory quantitative solution to the problem of the luminescent-photographic method of spectrophotometry, it was necessary in the elaboration of the method to fulfill the following conditions:

1. The methods of spectrography, the apparatus and the treatment of the photographic plates must remain the ordinary ones. This can be carried out most simply by a method of contact photography, using a luminescent screen pressed closely to the photographic plate used in spectrography.

2. The light emission of the fluorescent screen must be close to unity, so as to avoid considerable losses in the sensitivity of the apparatus and the great lengthening of the exposure connected with this.

3. The complete absorption of the light by the screen must be ensured in the whole of the ultra-violet region of the spectrum under examination.

4. The coefficient of absorption of the fluorescent solution must be considerably greater than the coefficient of absorption of the solvent and still more than the base on which the film is formed.

5. The spectrum of the fluorescence of the screen must lie in the region of the greatest spectral sensitivity of the ordinary slow plates used in photographic photometry.

6. The thickness of the fluorescent film must be as small as possible, so that the quality of the spectrogram (the sharpness of the image) remains as usual in direct spectrography.

7. The fluorescent screen must be stable, and above all stable to light, not disintegrating under the effect of ultra-violet rays. It must be made of long lasting or easily replaced material.

As practice has shown, all these conditions can be carried out with comparative ease.

For our work we used the universal spectrograph for chemists by Zeiss.

As a screen we used a thin gelatine film stained with a fluorescent substance, formed either on a quartz plate corresponding to the size of the photographic plates (9×12 cm^2), which was then placed with the film towards the emulsion of the photographic plate and inserted together with it in an ordinary plate holder, or were formed on a quartz plate sized 1×10 cm^2, which was attached to the frame like the folding frame of the wave length scale in spectrography.

The latter method was extremely simple and convenient. Firstly, it did not require big quartz plates, and, secondly, it makes it possible to place the screen in the beam only at the desired moment Thirdly, if the adjustment of the screen is sufficiently good, it makes it possible to work without changing the focussing of the spectrograph, if ordinary spectrographing is re-

quired. The springs of the photographic slides in which the plate is placed ensure that the screen will be pressed tightly against the photographic plate.

The fluorescent substance chosen for the screen was sodium salicilate which has a good emission of light and a suitable spectral absorption in the region 2000 to 3600 Å.

Fig. 1 shows the curve of absorption of a water solution of gelatine, obtained under the same conditions as for the solution of sodium salicilate in water. As can be seen from a comparison of the curves, the coefficient of absorption of sodium salicilate is considerably in excess of the coefficient of absorption of gelatine.

The absence of concentration quenching in a gelatine solution of sodium salicilate makes it possible to prepare films with a great concentration of this substance ($1 \cdot 10^{-2}$ g/cm³), thus ensuring complete absorption in a comparatively thin layer of film (20—30 μ). The spectrum of the fluorescence of sodium salicilate lies in the region of the blue, with a maximum about 4500 Å, which satisfies the above-mentioned fifth condition.

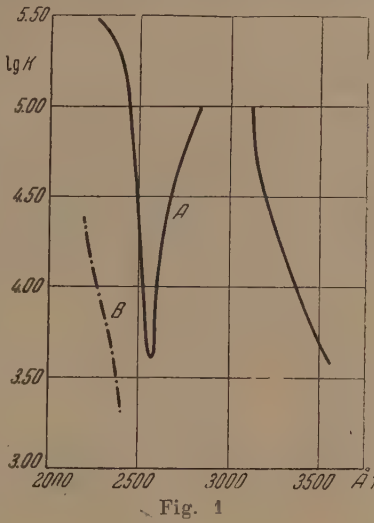

Fig. 1

The quality of the prints of the spectrograms obtained by means of the fluorescent screen is considerably below the quality of ordinary spectrograms in direct spectrographing.

The recipe for preparing the fluorescent film of acid sodium salicilate is exceedingly simple: 1.5 cm³ of an aqueous solution of sodium salicilate having a concentration of $5 \cdot 10^{-1}$ g/cm³ is mixed with 3 cm³ of an aqueous solution of gelatine having a concentration of $1.5 \cdot 10^{-1}$ g/cm³, and heated to the temperature of 40—50° C. Then the mixture, having a volume of 4.5 cm³, is poured on to the carefully cleaned surface of the quartz plate which is laid down horizontally. One tenth of the above-mentioned quantity is needed for a plate of 1×10 cm². The films are dried at ordinary temperature for 20—30 hours.

After the films dry, the «bloom» which appears owing to the surface crystallization of the sodium salicilate is washed away with warm water by dipping the plate into a bath for 5—10 seconds and drying the film once more. As the result, we obtain an absolutely transparent uniform film of sodium salicilate on quartz, cemented, as it were, by an insignificant quantity of gelatine. Such a screen is stable enough, and if covered by a protecting layer of transparent varnish, collodion for example, it will last a long time. No signs of its disintegration under the effect of ultraviolet rays were discovered after lengthy use. Before being used, the screen was tested for full absorption by an exposure which several times exceeds the exposures used in photographing a spectrogram.

In order to make a quantitative test of the method of spectrophotometry which we propose, we decided to measure the distribution of the energy in the spectrum of a hydrogen lamp. As we know from the work of Chalonge ([4]), the continuous spectrum of hydrogen does not depend very greatly on the conditions of excitation, pressure and construction details of the tubes.

Winans and Stuecelberg (5) theoretically calculoted the distribution of energy in the continuous spectrum of hydrogen, while Chalonge, by an ordinary photographic method, experimentally measured its parts lying in the long-wave region, and his results coincided within certain limits with the theoretical calculations.

In our experiments, the spectrophotometry was conducted as follows. A number of spectrums of the hydrogen lamp were taken one after another with the same exposure and with a suitable weakening of the light of the hydrogen lamp by means of photometric nets of known transparency.

Then, according to the impressions obtained, a series of curves of the blackening of the photographic plates was constructed. By these curves, the relative distribution of energy in the spectrum of the hydrogen lamp was determined from the equation:

$$\frac{E_{\lambda_0}}{E_{\lambda_n}} = \frac{I_{\lambda_0}}{I_{\lambda_n}} \left(\frac{\lambda_n}{\lambda_0} \right)^4$$

where the correction for dispersion for a continuous spectrum is taken into account.

The results of the measurements are shown on Fig. 2, curve A. For the sake of comparison, we give here curve B according to the figures of Chalonge showing the distribution of energy in the spectrum of the hydrogen lamp which he obtained by the ordinary photographic method. As a standard of comparison he used the crater of a voltaic arc. The curve A breaks off at a maximum about 2400 Å. As may be seen from the graph, both curves A and B practically coincide. In our measurements we used a Dunayet hydrogen lamp (p=10 mm of mercury column, V=3000), for which Chalonge gives the results of the measurements of the energy in the specrtum.

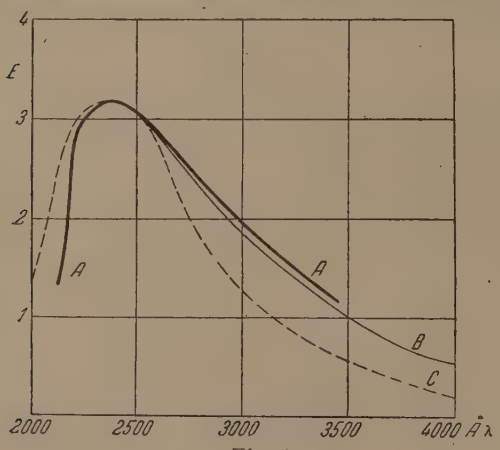

Fig. 2

The dotted line on the graph (Fig. 2) is the theoretical curve C calculated by Winans and Stuecelberg (5). Curves A, B and C overlap in their maximums, which, with a limit of error of 30 Å, lie in the region of 2400 Å, practically coinciding in all three cases. The theoretical curve C lies sufficiently close to the experimental curve A which we obtained. Thus the theory of Winans and Stuecelberg, which gives an explanation of the origin of the continuous molecular spectrum of hydrogen, obtains experimental confirmation. The complete coincidence of theoretical and experimental figures is in general hardly probable for incandescent gaseous sources of light, because the processes taking place in the luminescent gases are extremely complex and very frequently depend on the regime of burning and the design of the tube (6). On the other hand, the more rapid fall in the short-wave part of the branch of curve A may be explained by a certain absorption which undoubtedly takes place in this part of the optical system of the spectrograph. On the contrary, a

certain growth in the long-wave part of curve A as compared with the theoretical curve C may be caused by an admixture of diffused light.

Thus this method of spectrography in the ultra-violet region with the aid of a luminescent screen makes it possible to make quite satisfactory measurements of the relative distribution of energy in the spectrum. In addition, the screen may find application in the elaboration and perfecting of various methods of spectral analysis. For example, the visual method of Scheibe and Limmer which the authors worked out for the visible region of the spectrum can be transferred to the ultra-violet region as well. The method of homologous couples can be considerably extended. Absorption analysis in the ultra-violet region, which was left alone by the spectroscopists, may also be considerably improved with the aid of a hydrogen lamp and a luminescent screen.

In conclusion, we express our profound gratitude to S. I. Wawilow, under whose guidance this work was performed.

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13. VIII. 1937.

REFERENCES

[1] S. I. Wawilow, ZS. f. Physik, **42**, 311 (1937). [2] W. Fabrikant, Sow. Phys., **3**, 567 (1933); E. J. Bowen, Proc. Royal Soc., No 882, **154**, 349 (1936). [3] G. R. Harrison a. P. A. Leighton, J. O. S. A., **20**, 313 (1931). [4] D. Chalonge, Ann. de Physique, **1**, 169 (1934). [5] Winans a. Stuecelberg, Proc. Nat. Acad. Sc., **14**, 867 (1928). [6] A. Chevallier, P. Dubouloz et Henri Roux, Revue d'Optique, No 1, 28 (1937).

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PHYSICS

STUDY OF HEAVY PARTICLES IN COSMIC RADIATION AT A HEIGHT OF 4250 METRES ABOVE SEA-LEVEL

By V. VEKSLER and B. ISAJEV.

(Communicated by S. I. Wawilow, Member of the Academy, 11. IX. 1937)

By analysing the intensity curve of cosmic rays plotted against height, and some other data, some investigators have been led to assume the presence of heavy particles in cosmic radiation.

This hypothesis has been experimentally confirmed by the observations of Blackett (1), Street, Schneider and Stevenson (2), Brode, Macpherson and Starr (3), as well as by those of Anderson (4), who have succeeded in recording in a Wilson chamera traces of heavy particles, which can be accounted for by the action of cosmic radiation. The data obtained by Rumbaugh and Locher (5) in photographing the paths of particles in the emulsions of photographic plates lifted by the stratost, as well as the observations made by Anderson (6) on Pyke peak, warrant the conclusion that the intensity of heavy particles increases considerably with height. Still, the evidence so far available is of a purely qualitative and partly conflicting nature [thus, the data of Brode are at variance with the results obtained by Montgomery, Swann and Ramsay (7), while Clay's (8) observations are at variance with either]. At the same time, a detailed knowledge of the processes that are responsible for the appearance (origin) of such particles, their intensity, the variations of the latter with height, etc., can supply valuable information as to the nature of cosmic radiation and the nature of its unteraction with the atomic nuclei.

Having taken into consideration these circumstances, one of the writers working at the Physical Institute of the Academy of Sciences, has developed a method that makes it possible not only to ascertain the number of heavy particles passing through the apparatus but also to measure the ionization they produce.

This method was used by the writers to investigate heavy particles at a height of 4250 m above sea level when taking part in the Elbrus Expedition of the Academy of Sciences in the summer of 1937.

Brief Description of the Method

The experimental equipment used by the writers consisted of two groups of «proportional amplifiers» (9). Every group consisted of five proportional counters connected in parallel and placed in the same plane. The two groups were placed one above the other, the anodes of each of them being connected to the corresponding branches of the coincidence scheme. Johnson's scheme was used as the latter, but with a previous amplification in each circuit.

The arrangement described was thus absolutely similar to the usual coincidence schemes involving the use of Geiger-Müller counters, the only difference being that «proportional counters» were employed instead of the latter.

The above arrangement made it possible to study not only the heavy particles, but also the electronic (+ and —) showers. This question will be dealt with more fully in a separate notice.

Results of the Study of Heavy Particles

The measurement of the intensity of heavy particles was made by inserting iron gaskets, 0.75 or 1.5 mm thick, between the upper and the lower groups of proportional counters. For a space of 15 minutes the background was measured, i. e. the number of coincidences taking place with the gasket removed (denoted by N_{bg} in the tables), and in the next 15 minutes the number of coincidences occurring in the presence of the gasket was recorded (N_{Fe}). The results of the measurements are shown in Table 1.

Table 1

Notation	Number of coincidences	Duration of measurement	Number of coincidences per hour
N_{bg} coincidences with the gaskets removed	314	8 h. 50 m.	35.5
N_{Fe} coincidences with 0.75 mm iron gasket	143	7 h. 50 m.	18.24
$N_{bg} - N_{Fe}$ number of heavy particles	121	7 h. 00 m.	17.26
N_{bg} coincidences with the gaskets removed	218	5 h. 45 m.	37.8
N'_{Fe} coincidences with 1.5 mm iron gasket	90	5 h. 45 m.	15.6
$N_{bg} - N'_{Fe}$ number of heavy particles	128	5 h. 45 m.	22.2

The numbers of coincidences denoted by N_{bg} and N_{Fe} in the above table refer to such cases where no screens whatever were placed directly over the proportional counters. Experiments were also made with 3 mm aluminium or lead plates placed above the counters. The results of these measurements are shown in Tables 2 and 3.

Table 2

Notation	Total number of coincidences	Number of coincidences per hour	Duration of observation
N_{bg} coincidences with aluminium plates removed	109	12	8 h. 45 m.
N_{Al} coincidences with aluminium plates placed over the counters	100	11	9 h. 00 m.
Difference $N_{Al} - N_{bg}$	—9	—1	—

Table 3

Notation	Total number of coincidences	Number of coincidences per hour	Duration of observation
N_{bg} coincidences with no lead over the counters .	77	30	2 h. 34 m.
N_{Pb} coincidences with lead over the counters . .	103	40.8	2 h. 30 m.
N_{Pb+Fe} coincidences with lead over the counters and an iron gasket between the counters . . .	95	37.8	2 h. 30 m.
$N_{Pb}-N_{Pb+Fe}$ number of heavy particles due to lead . . .	8	3	—
$N_{bg}-N'_{Fe}$ number of heavy particles with no lead over the counters, borrowed from Table 1	—	22.2	—

As may be seen from Table 1, the placing of iron gaskets between the proportional counters reduces the number of coincidences by half. This can be easily accounted for the presence of strongly ionizing particles that are absorbed by the iron plates. The assumption that this may be traceable to showers is difficult to reconcile both with the small thickness of the absorbing metal and with the data of Table 3. If the iron gaskets did absorb some electron showers, an absolute increase in the number of the latter ought to have increased the percentage filtered by the iron. A direct examination of Table 3 shows, however, that, although the placing of lead over the counters causes the number of coincidences to increase, still the number of those filtered by the gaskets is incomparably smaller than it is in the experiments tabulated in Table 1. (The fact that, in the case of lead, the increase in the number of discharges ought to be attributed to showers of positive and negative electrons is also confirmed by Rossi's curve obtained by us by the same method. The curve will appear in a subsequent notice.)

An estimate of the ionization due to the particles filtered by the iron (calculated from the graduating curve of the sensitivity of the apparatus) shows their ionizing power to be about 10—15 times as great as that of the cosmic electron.

In spite of the fact that the recorded number of particles is not sufficiently large, the data obtained would seem to indicate that the placing of aluminium over the proportional counters does not increase the number of heavy particles. Table 2 shows that the number of coincidences in the presence of aluminium does not exceed their number in the absence of it. As, on the other hand, the placing of aluminium over the apparatus is known to increase the number of showers, it follows that aluminium does not emit heavy particles in any appreciable number*.

It has also been stated above that the increase in the number of coincidences was due to showers and not to heavy particles, even if lead had been placed above the proportional counters. If, therefore, the heavy particles

* In the experiments with aluminium, the sensitivity of the apparatus had been somewhat reduced in order to make it easier to differentiate between the heavy particles and the great showers.

recorded by us appear not simultaneously with showers the above data justify the conclusion that, in their case, there is no appreciable dependence on the atomic number of the radiating material. This problem is expected to be further elucidated by subsequent experiments.

In conclusion, we deem it a pleasure to place on record our profound gratitude to Academician S. I. Wawilow, for the interest he took in the work, for a number of valuable suggestions and the organization of the Expedition. We also thank D. V. Skobeltsyn for his valuable advice and suggestions in the course of the work. The writers also wish to express their gratitude to G. M. Frank, Chief of the Elbrus Expedition, and to N. A. Rayeva, Assistant Chief of the Scientific Section of the Expedition, for their constant help and attention to the work.

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Received
11. IX. 1937.

REFERENCES

[1] Blackett a. Occhialini, Proc. Roy. Soc., **139,** 699 (1933). [2] Street, Schneider, Stevenson, Phys. Rev., **48,** 436 (1935). [3] Brode, Macpherson, Starr, Phys. Rev., **50,** 581 (1936). [4] Anderson, Phys. Rev., **41,** 405 (1932). [5] Rumbaugh a. Locher, Phys. Rev., **49,** 855 (1936). [6] Anderson a. Neddermeyer, Phys. Rev., **50,** 263 (1936). [7] Montgomery, Ramsay, Swann, Phys. Rev., **50,** 403 (1936). [8] Clay, Physica, **2,** 111 (1935). [9] V. Veksler a. V. Isajev, C. R. Acad. Sci. URSS, III, 367 (1936).

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PHYSICS

SHOWERS STUDIED AT THE HEIGHT OF 4250 METRES ABOVE SEA-LEVEL

By V. VEKSLER and B. ISAJEV

(Communicated by S. I. Wawilow, Member of the Academy, 5. X. 1937)

The methods we used in the study of heavy particles of cosmic radiation have been described in our previous communication. It have been mentioned there, that the same methods are available for the study of the showers as well. We studied the latter during the Elbrus Expedition of the Academy of Sciences in the summer of 1937.

In the notice dealing with the heavy particles we pointed out (see Table 1) that nearly half a number of coincidences (the total being 35—36 per hour)

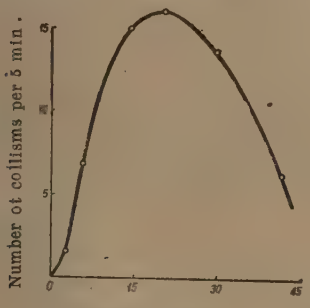

Fig. 1

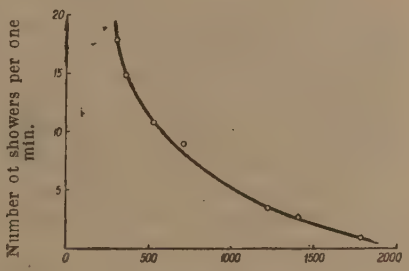

Fig. 2

was due to particles readily traversing a 3 mm lead plate. The assumption that those coincidences are due to showers, have been supported by the study of the dependence of the number of coincidences upon the thickness of the lead screen situated over the both groups of proportional amplifiers. We have plotted the curve represented in Fig. 1, which is evidently a curve of Rossi. It essentially differs from the curves obtained on the sea-level in its maximum being shifted towards the great thicknesses. This effect, however, was displayed by Gilbert ([1]), who examined the showers on the Jungfraujoch by means of usual counters. The shower-like nature of the particles producing coincidences due to lead, is supported as well by the dependence established by us of the number of ionization collisms upon their magnitude.

This dependence was made out by measuring the number of coincidences with an apparatus of varying sensitivity*.

The result of the differentiation of the integral curve thus obtained (Fig. 2) is shown in Fig. 3.

The number of electrons in the shower immediately calculated from the value of the collism should be somewhat arbitrary as the path of the particles is unknown. Assuming the showers to diverge inconsiderably, one may evaluate the collism as due to 3—4 electrons. In this case the

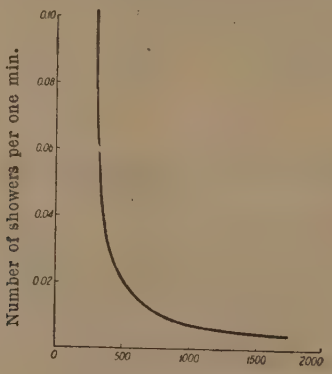

Fig. 3

curve in Fig. 3 affords a probability for the appearance of the showers with a given number of particles.

Such evaluation is supported by a comparison of our numerical data with those obtained by Street and Yong[2] in their works on the air—lead transition effect, carried on at the same height, as well as with the statistics of paths afforded by the camera of Wilson.

Thus one may put down the collisms produced by slightly absorbable particles to the showers of electrons and positrons.

This proves the methods suggested to be a real means for studying the different components of cosmic radiation.

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5. X. 1937

REFERENCES

[1] Gilbert, Proc. Roy. Soc., **144**, 559 (1934). [2] Street a. Yong, Phys. Rev., **47**, 572 (1935).

* By means of subsequent graduation there was established the minimal number of the ion pairs which ought to be created to produce coincidence.

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PHYSIQUE DU GLOBE

LES PROPRIÉTÉS DE LA LUMIÈRE DIFFUSE DU CIEL

Par I. A. KHVOSTIKOV

(Présenté par S. I. Wawilow, de l' Académie, le 4. VII. 1937)

1. Au mois de mars 1936 l'auteur s'est élevé 2 fois en substratostat à la hauteur de 8—10 mille mètres pour étudier les propriétés de la lumière diffuse du ciel.

À la première ascension le substratostat atteignit la hauteur de 9450 m (9 mars). Le substratostat était piloté par le lieutenant B. A. Romanov. À la seconde, piloté par le colonel G. A. Prokofiev, il atteignit une hauteur de 7900 m.

Pendant ces deux ascensions on déterminait la répartition de l'énergie dans le spectre de la lumière diffuse du ciel et le degré de polarisation de cette lumière dans les différentes régions du spectre. Notre méthode nous permettait d'obtenir l'un et l'autre simultanément.

Il a suffit pour cela d'un leger changement de construction du spectrographe: on introduit dans le tube à colimateur du spectrographe, entre la fente et le verre objectif, une plaque cristalline à double réfraction, ce qui permet d'obtenir sur la photographie deux spectres polarisés l'un au-dessus de l'autre. L'un de ces spectres correspondait au rayon ordinaire et l'autre—au rayon extraordinaire. Grâce aux lignes sombres d'absorption portées d'avance sur la plaque, on pouvait calculer la répartition de l'énergie dans chacun des deux spectres. Si $I_{\lambda\perp}$ est l'énergie correspondant à la longeur d'onde λ dans le premier des deux spectres (en unités arbitraires) et $I_{\lambda\parallel}$ est l'énergie correspondant au second, leur somme $I_{\lambda\perp} + I_{\lambda\parallel}$ peut représenter la mesure de l'énergie pour l'onde de longeur λ et la relation $p_\lambda = \frac{I_{\lambda\perp} - I_{\lambda\parallel}}{I_{\lambda\perp} + I_{\lambda\parallel}}$ permet d'obtenir le degré de polarisation de la lumière diffuse pour la longeur d'onde λ.

2. Deux spectrographes ont été utilisés pour la prise des clichés. L'un d'eux était assez lumineux (près de $f/2.5$) mais peu dispersif et la longueur du spectre visible de 400 à 600 mμ ne dépassait pas 12 mm. Le deuxième spectrographe était de beaucoup moins lumineux, mais formait un spectre d'environ 7 cm pour l'intervalle des longueurs d'onde indiqué.

On photographiait des marques de noircissement, fournies par une lampe à incandescence dont on avait déterminé la répartition dans le spectre de l'énergie lumineuse pour différentes températures, ce qui procura un point de départ pour l'étude de la répartition d'énergie le long du spectre.

3. Nous avons obtenu trois spectrogrammes, deux à l'aide du spectrographe à grande luminosité à la hauteur de 9450 m le 9 mars entre midi et

13 heures, le troisième spectrogramme à la hauteur de 7900 m le 22 mars entre 14 h. 30 m. et 15 h. 30 m. à l'aide du spectrographe à haute dispersion.

Les trois clichés ont été pris par un temps clair sans nuages, en dirigeant l'appareil vers la même partie du ciel, sous un angle de 45° avec l'horizon dans la direction de l'ouest.

La fig. 1 représente la répartition de l'énergie dans le spectre. Les ronds noirs (courbe *1*) présentent la moyenne obtenue après l'examen des trois

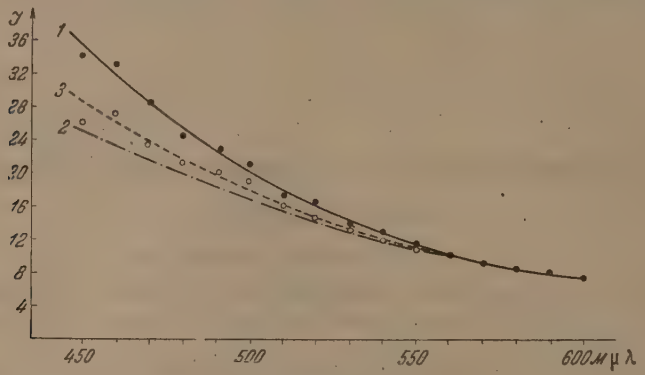

Fig. 1

spectrogrammes, qui d'ailleurs ont fourni des résultats coïncidants (voir la colonne 2 du tableau 1).

La fig. 2 présente les résultats des mesures du degré de polarisation. La courbe *1* est tracée d'après les photos du 9 mars et la courbe *2*—d'après celles du 22 mars.

Tableau 1

1 λ en mμ	2 $I_{exp.}$	3 $I_{Rayleigh}$	4 $I_{corr.}$	5 $P_{exp.}$ 9. III 1936	6 $P_{exp.}$ 22. III 1936
450	34.2	25.2	26.2	55.2	48.2
460	33.1	23.4	27.2	59.1	50.5
470	28.2	21.6	23.4	59.6	53.7
480	24.5	19.9	21.5	63.2	52.7
490	22.7	18.1	20.5	63.6	54.4
500	21.2	16.7	19.2	64.9	56.4
510	16.9	15.2	16.1	68.9	58.0
520	16.2	13.8	14.5	65.6	59.7
530	13.7	12.6	13.1	68.5	58.3
540	12.6	11.4	11.9	67.8	58.4
550	11.1	10.4	10.8	70.5	60.2
560	9.9	9.4	9.6	69.7	61.0
570	8.8	8.5	8.7	72.0	58.4
580	8.1	7.8	8.0	69.0	60.7
590	7.9	7.1	7.4	72.0	62.0
600	6.9	6.6	7.2	71.9	61.9

4. Pour faciliter la comparaison on a tracé (fig. 1) la courbe théorique de la répartition de l'énergie dans le spectre, en admettant d'après Rayleigh la proportionnalité entre le coefficient de la dispersion de lumière et l'inverse de la quatrième puissance de la longueur d'onde. Les données concernant

la répartition de l'énergie dans le spectre du soleil étaient empruntées à Abbot et extrapolées au delà des limites de l'atmosphère (1).

La comparaison de la courbe théorique (*1*) avec la courbe expérimentale (*2*) montre que la lumière diffuse de l'atmosphère est plus riche en rayons bleus qu'il n'en résulte de la loi de Rayleigh. L'échelle des ordonnées est construite de sorte que la valeur de l'énergie correspondant à $\lambda = 600\,m\mu$ est la même pour les deux courbes.

Si l'on exprime la loi de diffusion de la lumière par la formule $I \sim \frac{I_s}{\lambda^n}$ (I_s, valeur de l'énergie dans le spectre du soleil), d'après laquelle le coefficient de la dispersion est inversement proportionnel à la n-ième puissance de la longueur d'onde, on obtient pour la courbe expérimentale $n = 5.3$ au lieu de $n = 4$ qui résulte de la loi de Rayleigh.

5. Les courbes de la fig. 2 montrent comment varie la polarisation dans le spectre de la lumière diffuse: on observe une diminution sensible du degré de polarisation dans la partie bleue du spectre. La courbe de polarisation, obtenue le 9 mars (*1*) passe un peu plus haut que la courbe (*2*) du 22 mars.

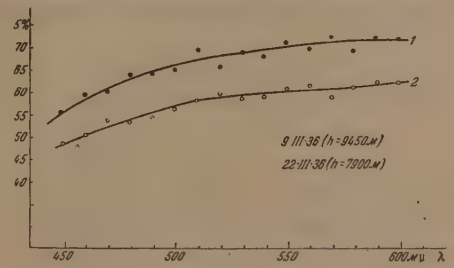

Fig. 2

Cette différence entre les puissances de polarisation n'est pas due à la hauteur, mais probablement à la rotation continuelle de l'aérostat. Les expériences du 22 mars étaient effectuées en présence d'un vent très fort et dès le départ l'aérostat subissait un mouvement de rotation rapide. Celle-ci était encore sensible (1 tour 2—3 sec.) quand l'aérostat atteignit sa hauteur maximum.

Pour maintenir la direction du spectrographe constante il fallait compenser le mouvement de rotation du stratostat par un mouvement de sens inverse du trépied. Il était impossible de maintenir exactement la direction voulue (formant un angle de 90° avec le soleil), ce qui entraînait une diminution du degré de polarisation.

D'ailleurs l'allure des deux courbes le long du spectre est la même partout; on observe une diminution de la polarisation dans la partie bleue du spectre.

6. Les phénomènes que nous avons observés peuvent être expliqués de la manière suivante.

La diminution de polarisation de la lumière diffuse du ciel dans la partie bleue du spectre peut être due à la diffusion secondaire de la lumière. En effet la dispersion secondaire doit être complètement dépolarisée. Si la dispersion secondaire présente une valeur importante, son action doit tout d'abord affecter la partie du spectre à ondes courtes, car si l'intensité de la dispersion primaire est inversement proportionnelle à la quatrième puissance de la longueur d'onde, l'intensité secondaire est inversement proportionnelle à la huitième puissance de la longueur d'onde.

Outre la diminution relative de la polarisation dans la partie bleue du spectre, la dispersion secondaire doit affecter aussi la composition spectrale de la lumière diffuse. Comme la dispersion purement secondaire est inversement proportionnelle à la huitième puissance (et non pas à la quatrième) de la longueur d'onde, nous devons obtenir pour la dispersion mixte (primaire et secondaire) de la lumière un exposant n compris entre 4 et 8. Ainsi s'explique l'exposant 5.3 que nous avons trouvé.

Voici quelques calculs numériques. Supposons que la diminution du degré de la polarisation dans la région bleue du spectre (à ondes courtes), que l'on observe sur les courbes de la fig. 2, comparée à celle de la région rouge du spectre est due entièrement à la dispersion secondaire de la lumière. Autrement dit, admettons que la dispersion primaire donne le même degré de polarisation pour toutes les longueurs d'onde et qu'après exclusion de la diffusion secondaire le degré de la polarisation doit être égal à $p' = 72\%$, pour $\lambda = 450$ mμ aussi bien que pour $\lambda = 600$ mμ.

On observe en réalité une polarisation de $P = 55\%$ seulement.

Proposons nous de déterminer ce qu'il faut exclure de lumière disperse secondaire pour obtenir un degré de polarisation égal à 72%? L'énergie de la lumière disperse à la longueur d'onde $\lambda = 450$ mμ se compose de deux parties: $I = I_\perp + I_\parallel$ (voir 1.), qui déterminent le degré de polarisation:

$$P = \frac{I_\perp - I_\parallel}{I_\perp + I_\parallel}.$$

Excluons l'énergie lumineuse due à la dispersion secondaire. Nous obtenons: $I'_\perp = I_\perp - \Delta I$ et $I'_\parallel = I_\parallel - \Delta I$, ΔI est le même dans ces deux cas, parce que la dispersion secondaire est dépolarisée. La valeur numérique du degré de polarisation corrigée devient:

$$p' = \frac{I'_\perp - I'_\parallel}{I'_\perp + I'_\parallel} = \frac{I'_\perp - I'_\parallel}{I'},$$

où $I' = I'_\perp + I_\parallel$. Mais $I'_\perp - I'_\parallel = I_\perp - I_\parallel$, et à son tour $I_\perp - I_\parallel = P \cdot I$, c'est pourquoi $p' = \frac{P \cdot I}{I'}$, d'où nous obtenons l'expression pour l'énergie corrigée:

$$I' = I \frac{P}{p'}.$$

Les données corrigées au moyen de cette formule sont présentées dans le tableau 1 (colonne 4) et sur la fig. 1 (courbe *3*). La courbe corrigée passe beaucoup plus près de la courbe théorique et donne $n = 4.4$. Mais il existe encore une certaine divergence entre les deux courbes.

7. En discutant les résultats cités plus haut S. I. Wawilow, de l'Académie, a remarqué que si l'on veut tenir compte de la lumière secondaire dépolarisée, il est indispensable non seulement de tenir compte de deux composantes $I_\perp$ et $I_\parallel$, mais aussi de la troisième composante suivant le rayon visuel, qui n'est pas perçue directement par l'observateur, mais retient une certaine quantité d'énergie. La dispersion secondaire, étant dépolarisée, doit donner trois composantes égales, et si nous avons antérieurement supposé que $I' = I'_\perp + I'_\parallel = I - 2\Delta I$, nous devons obtenir maintenant, après exclusion complète de la dispersion secondaire, $I'' = I - 3\Delta I$.

Tableau 2

Longueur d' onde en mμ	I'' corrigé définitivement	Selon Rayleigh I
450	22.2	25.2
460	24.3	23.4
470	21.0	21.6
480	20.0	19.9
490	19.4	18.1
500	18.2	16.7
510	15.7	15.2
520	13.7	13.8
530	12.8	12.6
540	11.6	11.4
550	10.6	10.4
560	9.4	9.4
570	8.6	8.5
580	7.9	7.8
590	7.2	7.1

Les valeurs calculées d'après cette formule sont réunies dans le tableau 2 de même que les valeurs correspondant à la formule de Rayleigh.

La fig. 3 représente une courbe théorique correspondant à la formule de Rayleigh, et les valeurs expérimentales corrigées I'' sont représentées par des cercles. La coïncidence est complète.

8. Cette coïncidence est probablement due au hasard, car la mesure photographique de l'intensité de la lumière présente, comme on le sait, une erreur beaucoup plus grande (10—15%) que la différence entre nos valeurs et celles de la courbe de Rayleigh. Mais les trois spectrogrammes ayant donné indépendamment des résultats identiques, on peut admettre l'explication donnée plus haut à savoir le rôle que la diffusion secondaire de la lumière dans l'atmosphère joue dans la répartition spectrale de la polarisation. On peut donc utiliser les courbes de répartition et en tirer les valeurs de la diffusion secondaire dans les différentes régions du spectre.

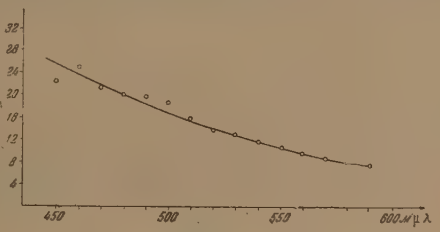

Fig. 3

L'auteur présente ses remerciements à S. I. Wawilow, de l'Académie, d'après l'initiative duquel ont été organisées ces expériences, pour son attention aux travaux et pour ses indications précieuses. L'auteur remercie aussi sincèrement le colonel G. A. Prokofiev d'avoir concouru à l'organisation de ces travaux et d'avoir créé d'excellentes conditions pour les observations scientifiques dans la stratosphère, ainsi que pour sa participation personnelle à ces expériences.

Commission d'Étude de la Stratosphère.
Institut Optique de l'État.
Académie des Sciences de l'URSS.

Manuscrit reçu
le 4. VII. 1937.

LITTÉRATURE CITÉE

[1] G. G. Abbot, Ann. Rep. Smiths Inst., 62 (1911); G. G. Abbot, F. E. Fowle a. L. B. Aldrich, Smith Misc. Coll., **79**, No 7 (1923).

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GÉOCHIMIE

ÉTUDES DANS LE DOMAINE DE LA COLORATION DES MINÉRAUX

Par A. E. FERSMAN, de l'Académie

La coloration en présence des ions de différente valence

1) La nature de la coloration des minéraux n'a été étudié que très insuffisamment et la différence de coloration entre les minéraux naturels et les composés artificiels est jusqu'à présent restée inexpliquée.

Tandis que la coloration allochromatique est étudiée avec un grand succès à l'Institut Optique à Leningrad, la coloration idiochromatique qui est liée avec la structure du réseau cristallin, reste entièrement inétudiée et même n'a pas été décrite.

Cependant l'importance de la coloration typique des composés naturels en minéralogie, géochimie et géologie s'accroît chaque année et la couleur d'un minéral et d'une roche devient un trait diagnostique le plus important dans les recherches des minerais (1).

2) Dans cette note je m'arrête sur un phénomène bien caractéristique qui a une grande expansion et qui peut avoir une grande importance dans la chimie préparative. C'est l'enfoncement (l'abaissement) de la coloration d'un composé, lorsque dans son réseau entrent les ions du même élément, mais avec les divers degrés de ionisation ou de valence (2)*.

Cet abaissement de la couleur est lié avec l'absorption des ondes plus longues (jaunes ou orangées, de préférence) et avec le renforcement de l'absorption totale, en conséquence de quoi l'on obtient des composés de couleur sombres: bleu ou bleu-violet, noir, semi-métallique et même de vrais systèmes métalliques avec un lustre et d'autres propriétés métalliques. Simultanément l'on observe l'apparition du paramagnétisme et de la conductibilité électrique.

L'explication de ce phénomène caractéristique ne peut encore être donnée d'une manière précise, mais il est évident qu'il est lié avec une incertitude dans l'état des nuages de valence qui surgit sur les confins de deux ions de charge différente et qui est suivie d'un déplacement aisé des électrons sur leurs niveaux énergétiques. Cette explication résulte entière-

* Nous donnons la succession des teintes d'abaissement: le spectre *B*—en conséquence du déplacement des bandes d'absorption vers les ondes longues (les composés artificiels purs): jaune-verdâtre, jaune, orangé, rouge, pourpre violet, indigo, bleu, bleuâtre-vert, vert. Le spectre *A*—en conséquence d'une extension des bandes du côté des ondes longues et d'un renforcement de l'absorption totale (surtout dans les corps minéraux naturels): gris, jaune-verdâtre, jaune-sale, orange-sale, fauve-rouge, rouge-fauve, brun foncé, noir, métallique d'acier et métallique d'or.

ment de nos ideés sur les causes de la coloration des composés naturels.

3) Dans les corps naturels nous observons ce phénomène si l'on a dans le même réseau les ions suivants:

$$Fe^{+2} + Fe^{+3}, \quad Mn^{+2} + Mn^{+3}, \quad Co^{+2} + Co^{+3}, \quad V^{+4} + V^{+5}.$$

Il est bien probable que l'étude ultérieure augmentera cette liste des couples, qu'on observe dans la nature, mais certainement la plus grande importance appartient au couple du fer qui joue en géochimie un rôle tout à fait unique (3).

Nous savons que l'entrée dans un réseau du fer protoxyde mène ordinairement à une coloration faible, jaune-verdâtre et par une abréviation conventionnelle nous pouvons parler d'un ion jaune-verdâtre, Fe^{-2}; également l'ion Fe^{+3} est caractérisé dans une série des ses composés (mais non pas dans tous) par sa couleur rouge-fauve, tandis que l'anion complexe qui joue en minéralogie un rôle très important, $[Fe_2O_4]^{-2}$ ou $[Fe\ O_4]^{-5}$, est caractérisé par sa belle couleur—pomme-verte.

La combinaison du fer bivalent et trivalent dans le même réseau mène pratiquement aux minéraux bleu foncé ou noir, d'une nuance fauvâtre ou, plus souvent, d'un éclat bleuâtre.

Suivant la proportion des deux ions on obtient des nuances bleues différentes jusqu'aux teintes métalliques noires.

En effet, nous pouvons nommer une série entière des minéraux qui suivent cette règle. Ainsi spécifiquement noirs sont: la mélanite (le grenat de calcium avec du fer protoxyde et oxyde), la grandidiérite, l'ilvaïte, la moravite, la taramellite, le schorl noir, l'orthite, la cronstedtite, la thuringite*, la babbingtonite, la lépidomélane (l'énigmatite), la série des amphiboles (la hornblende basaltique, arfvedsonite, etc.) et l'augite**.

Le minéral, le plus typique de caractère métallique dans ce groupe est, certainement, le magnétite. Parmi les autres groupes nous nommons les borates noires (la ludwigite) et, particulièrement, la série des phosphates, parmi lesquels nous avons toutes les transitions du bleu au noir. Tels sont les minéraux oxydés: la triplite, la vivianite, etc***.

A côté des minéraux noirs nous avons une large liste des corps minéraux bleus, qui sont en général très rares, mais qui avec le cuivre indiquent le plus important chromophore bleu en minéralogie. Tels sont, de la région des silicates les hornblendes alcalines, la glaucophane, la riebeckite, la crossite, la ternovskite, la hastingsite, la rhodusite, la crocidolite, la torendricite, partiellement l'arfvedsonite, etc.

Dans tous ces minéraux nous avons la substitution d'une part d'aluminium dans ses tétraèdres par le fer trivalent (l'oxyde de fer) et par conséquent la cinquième valence superflue nécessite la neutralisation du réseau par l'introduction d'un ion de sodium monovalent. C'est ainsi que la cause de la coloration n'est pas la présence du métal alcalin, mais la présence simultanée dans le même réseau du fer bivalent et trivalent (protoxyde et oxyde). Très intéressant est le groupe des phosphates bleus qui présentent toutes les transitions d'incolore jusqu'au fauve-noir à travers des composés bleu et bleu-violet foncé.

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*Probablement, nous pouvons placer ici la hisingerite, qui contient la couple Fe_2O_3+FeO (jusqu'à 6 pour cent FeO).

**J'ai omis dans cette liste intentionnellement les composés qui contiennent le titane, car la présence de cet élément conduit immédiatement à l'abaissement de la coloration, ce qui est dû, peut-être, à la présence simultanée du titane trivalent et tétravalent.

***Nous pouvons ajouter encore les borostannates, comme la hulsite, la paigéite, etc.

Cette série d'oxydation a été étudiée sur les vivianites dans le gisement des minerais de fer à Kertch par S. K. Popoff, et en 1937 la même série a été décrite par Quensel parmi les pégmatites de Suède. Tels sont les minéraux de la série de la lazulite, triplite, triphillite, etc. (4).

Un bel exemple de ces formations bleues donnent les fleurs terreuses sur les feldspaths des pégmatites de Mourzinka.

Ainsi nous pouvons voir que la combinaison dans une même série du fer bivalent et trivalent mène à une coloration bleue caractéristique, le fait qui a été déjà signalé par N. S. Kurnakoff, de l'Académie.

Ces teintes bleues ont trouvé une application large dans les verres aux laboratoires de l'Institut des Silicates de Prof. W. Eitel près de Berlin.

Quant aux combinaisons des ions divers des autres éléments dans les minéraux nous avons des indications comparativement exiguës pour le cobalte, le manganèse, le vanadium et l'uranium. Ainsi le manganèse donne la couple $Mn^{+2}+Mn^{+3}$ et nous obtenons une série des fauve-noirs avec un éclat métallique brownites ou hausmannites. Avec le vanadium $V_2O_4+V_2O_5$ nous avons un minéral noir—la corvusite ($V_2O_4 \cdot 6\ V_2O_5 \cdot xH_2O$).

Avec l'uranium nous avons un minéral noir—l'uraninite, qui correspond à la formule $UO_2+2UO_3=U_3O_8$. Enfin, avec le cobalte on a trouvé pendant ces dernières années en Congo Belgique un minéral pèche-noir, qui correspond à un composé résineux colloidal $Co_3O_4=CoO+Co_2O_3$.

4) Ce phénomène doit-être encore plus répandu en chimie et surtout en chimie préparative, ou nous rencontrons dans le même réseau des ions de différents degrés de valence avec les éléments suivants:

Fe, Mn, Co, Cu, V, U, W, Mo, Sn, Pb, Tl, As, Sb, Re, Cr.

Cela est apparent avec les exemples des composés artificiels, notés au bas de cette page, dont une série ne se produit que temporairement au cours d'une réaction d'oxydation ou de réduction*. Le phénomène de noircissement fort ou de bleuissement des solutions dans les stades initials des processus d'oxydation ou de réduction constitue un trait caractéristique qui a été plus d'une fois accentué dans la littérature [H. Remy (5)]. Dans ces cas nous obtenons en conséquence d'une combinaison des ions de valence différente: 1) des composés caractéristiques noir ou noir-violet, 2) ou bien semi-métallique avec des propriétés typiques des métaux, 3) ou, enfin, bleu vif, qui joue un rôle considérable dans l'industrie**.

Parmi les premiers nous devons placer la combinaison du fer trivalent et tétravalent, qu'on obtient pendant la réduction des sulphates dans le stade initial du procédé. Les teintes violettes des composés naturels, qui contiennent le titane, correspondent sans doute à la transition aisée de Ti^{+4} en Ti^{+3} qui se passe dans la nature. L'analyse énergétique des ions de titane montre que la différence des énergies des deux ions dans l'état fondu n'est pas grande et, par conséquent, les transitions mutuelles s'accomplissent suivant les moindres variations de la température.

Plus intéressant est le second groupe des composés, parmi lesquels se trouvent les célèbres bronzes de tungstène (sur lesquels mon attention a été appelée par O. E. Zvjagincev).

Au fur et à mesure d'augmentation de WO_2 aux dépens de WO_3 nous apercevons un enfoncement de la coloration(6). Un intérêt tout à fait excep-

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*$Fe(OH)_2+Fe(OH)_3$—verdâtre-jaune+rouge-fauve → noir (avec vert).
$Tl(OH)+Tl(OH)_3$—jaune-clair+rouge-fauve → noir.
$Sb_2O_3 \cdot H_2O+Sb_2O_5 \cdot H_2O$—incolore+incolore → fauve-noir.
UO_2+UO_3—brun+orange-jaune → noir U_3O_8.

**Les autres teintes sont très rares, par exemple, le rouge Pb_3O_4.

tionnel présente enfin par un large groupe des colorants bleus, dont plusieurs membres sont très stables et sont employés dans l'industrie. Tels sont les combinaisons:

le bleu de tungstène — $WO_3 + WO_2$,
le bleu de vanadium — $V_2O_3 + V_2O_5 (= V_2O_4)$,
le bleu de molybdène — $Mo_2O_3 + Mo_2O_5$ (?),
le bleu de rhénium — $ReO_3 + ReO_2$,
le bleu de cérium — $Ce_2O_3 — 2CeO_2 (= Ce_4O_7)$.

Les colorations même du Bleu de Prusse et dé Bleu du Turnbull peuvent être placées dans ce groupe de phénomènes, vu la présence différente dans tous ces cas les ions du fer de valence.

5) Il est évident que la région de tels composés colorés ou semi-métalliques est très vaste et qu'en partant des exemples cités et se basant sur des investigations cristallochimiques nous saurons obtenir un très grand nombre de composés de ce type avec les autres éléments, surtout avec Mo, Re, Sn,Ce, Ti, V, Cr, U, Tl et Pb.

Par analogie avec la dobréelite ($CrS + Cr_2S_3$—un minéral avec des propriétés magnétiques et métalliques qui se trouve parmi les minéraux de météorites) ce type de composés peut être obtenu non seulement des oxydes, mais aussi des complexes de soufre.

L'importance de ce type n'est pas tant dans la coloration que surtout dans ses propriétés magnétiques et celles de conductibilité qui de même que ses belles couleurs dépendent du réseau cristallin de ces composés et de la distribution de leurs niveaux énergétiques.

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LITTÉRATURE CITÉE

[1] А. Ферсман, Цвета минералов, Научн. сер. А. Н., 1—156 (1937). [2] W. Biltz, ZS. f. anorg. Chemie, **127**, 169—186 (1923). [3] S. Kolbe. Neues Jahrb. f. Min. **69** (A), 185—245 (1935). [4] P. Quensel, Geol. För. Förh Stock., **59**, 77—96 (1937). [5] Г. Реми, Учебн. неорг. хим. (перевод), II, 11—90 (1935). [6] В. И. Спицын, Журн. Русск. физ.-хим. о-ва, 474 (1926).

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BIOPHYSICS

ON THE COEFFICIENT OF DYING OUT OF COCKCHAFER LARVAE UNDER THE ACTION OF ELECTRIC CURRENT

By S. I. TURLYGIN

(Communicated by P. P. Lazareff, Member of the Academy, 25. VIII. 1937)

It is possible to prove the existence of a biological action of electric current either by means of a detailed biological analysis consisting in the observation of different changes taking place in the organism, or by means of an examination of the total (integral) effect, taking into account all the electric values.

The latter method is especially convenient if we have to deal with harmful insects and if the final result is to be the perishing of these insects. It is not always necessary, however, to bring this direct action to the lethal end. In order to reduce the consumption of power, it is possible to produce a more or less severe electrical trauma, which later on will result in the death of the insects. That such a trauma is possible is demonstrated in Lugovoj's paper (1), where it is said that the larvae of a cockchafer once exposed to the action of an electric current of ultra-high frequency perish gradually on the 30th or 40th day. In fact, if we expose a larva to even a comparatively weak action of ultra-high frequency, we observe that some changes take place in it; the larva becomes two or three times smaller in size, as if drying up, and at last perishes.

An especially convenient method for the observation of this electrical trauma is the registration of the number of individuals dead or still alive. The resulting record allows us to apply mathematical analysis to the study of this phenomena, which makes it possible not only to find the most convenient and the cheapest method for the extermination of parasites, but also to investigate some biological effects and their relation to some physical factors.

The contamination of soil by the cockchafer larvae is so great, in our country as well as abroad, that it has become a real scourge and is further aggravated by the fact that the struggle with it is very difficult and the methods of this struggle have not yet been worked out.

In the search for a convenient and economical method of solving this problem, the author thought it necessary to investigate the destructive action not only of the current of ultra-high frequency but also of the usual industrial current, which is very convenient due to its availability.

The cockchafer larvae were exposed to the action of the electric current in the following way. Plate-electrodes were inserted into the earth (sandy soil); between these electrodes some larvae were buried in different places.

The plates were connected to a 6600 V (effective) transformer for a time of 1 to 3 seconds. Electric current lines taken with a hydraulic model at different positions of the larvae are shown in Fig. 1. The measured density of the current in a «cupper» larva while in the second position exceeded the average current density in the ground about 12 times.

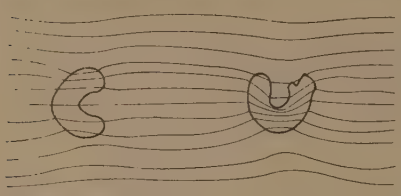

Fig. 1. Current lines passing through the larvae.

After the passage of the current the larvae were examined. The state of the larvae varied with the conditions of the experiments. At the mean gradient between the plates of 1110 V (maximum) and at the exposure (t_{exp}) of 2 — 3 seconds, the larvae were killed completely, while being exposed for only 1 second, a considerable number of them remained alive. At the mean gradient of 835 V/cm and being exposed for 1—2 seconds, the greater part of them remained alive. At the gradient of circa 300 V/cm, the larvae did not perish whatever the exposure.

After the larvae had been exposed to the action of electric current, they were placed in boxes filled with earth, in con-

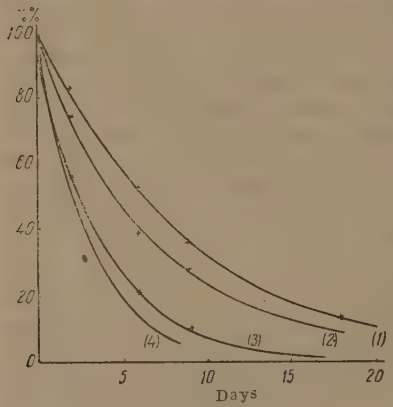

Fig. 2. % of live larvae.

(1) E=835V/cm $t_{exp.}$=1 sec.
(2) 835V/cm 2 sec.
(3) 1110V/cm 1 sec.
(4) 1180V/cm 1 sec.

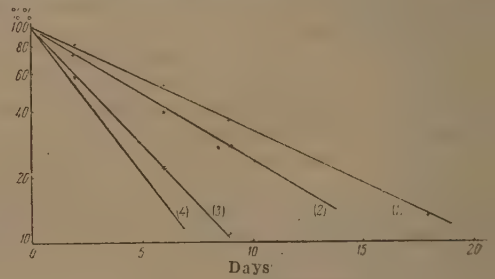

Fig. 3. % of live larvae.

(1) E=835V/cm $t_{exp.}$=1 sec.
(2) 835V/cm 2 sec.
(3) 1110V/cm 1 sec.
(4) 1180V/cm 2 sec.

ditions identical to their natural conditions, and from time to time the live larvae were counted. The results of the experiments are shown in Fig. 2. This figure shows that the percentage of larvae left alive is accurately determined by the exponential curve corresponding to the equation:

$$N = N_0 e^{-\alpha t} \qquad (1)$$

or in percentage,

$$100\left(\frac{N}{N_0}\right) = 100\, e^{-\alpha t}$$

where N is the number of live larvae observed in the time t, N_0 is the number of larvae at the first moment (at $t=0$), e is the basis of natural logarithms and α is a constant showing the rate of the dying out of the larvae, that is the coefficient of dying out. The larger α is the more rapidly will they perish.

The relation found will be more clearly demonstrated if we trace the experimental data on a logarithmic paper. This done, we receive straight

lines (Fig. 3), which confirm equation (1) because the logarithm of the ratio $\frac{N}{N_0}$ is a linear function of time. To show to what extent the experimental curve is close to the theoretical straight line, we may calculate the percentage of live larvae for the time t and compare it with the percentage of larvae observed at the same moment.

Then we have:

Table 1

Observed percentage of live larvae	83	53	36	13
Calculated percentage	79.8	50.8	36.2	13
Difference	3.2	2.2	1.2	0

Actually the coincidence will be considerably greater, as during the calculation of larvae the time was measured in days and not in hours. Consequently, there will be, of course, a somewhat greater mistake at small values of time. Table 2 will give the necessary values if we shift, say, the zero of time for 0.4 of a day.

Table 2

Observed percentage	83	53	36	13
Calculated percentage	82.2	52	36.7	13
Difference	0.8	1.0	0.7	0
The percentage of divergence from the theoretical value	0.9	1.88	1.9	0

The coincidence is very good.

At very small values of N the observed values differ from the theoretical curve. That is quite clear because, in this case, each larva constitutes a very noticeable part of the number left and the statistical method loses its accuracy.

In the following we shall assume that the zero is not shifted.

Thus, the exponential law:

$$N = N_0 e^{-\alpha t},$$

or (differentiating this equation)

$$dN = -\alpha N\, dt,$$

in the present case is quite exact.

On the basis of this law, we come to the conclusion that the change dN in the number of larvae (the number of dying larvae) will be always proportional to N, the existing number of larvae (the number of individuals), and to the coefficient α. This result is easily obtained by differentiating Eq. (1):

$$dN = -\alpha N dt$$

It is quite clear that the most important quantity, a quantity that governs the trend of this process, is the coefficient α, upon which depends the existing number of individuals at any moment of time. Every factor exercising a favourable or unfavourable influence on the organism by changing its conditions or its biological state will immediately produce a correspond-

ing change in α and affect the rate of dying out of these insects. Inversely, knowing the laws of dying out of the insects in different cases, we come to a conclusion concerning the nature of factors affecting the organism.

These considerations were used by the author in his investigation of the action of electric current on the cockchafer larvae. Applying the obtained curves, we may find the values of the coefficient α in all cases.

Its values are the following:

First curve, $E = 835$ V/cm; $t_{exp} = 1$ sec.; $N(\%) = 100 \cdot e^{-0.113t} \doteq$

$\doteq 100 \cdot 10^{-0.0494t}$;

$$\alpha = 0.0494;$$

Second curve, $E = 835$ V/cm; $t_{exp} = 2$ sec.; $N = 100 \cdot 10^{-0.062t}$;

$$\alpha = 0.062;$$

Third curve, $E = 1110$ V/cm; $t_{exp} = 1$ sec.; $N = 100 \cdot 10^{-0.113t}$;

$$\alpha = 0.113.$$

The curves and the obtained values show that the duration of the life of the larvae is influenced by the value of the gradient E and by the time of the action t_{exp}, i.e. the time of exposure. These are just the values which permit us to determine the power consumed during the experiments, which is proportional to the product $E^2 t_{exp}$. However, the total quantity of power used does not show whether the conditions of the experiment were rightly chosen or not.

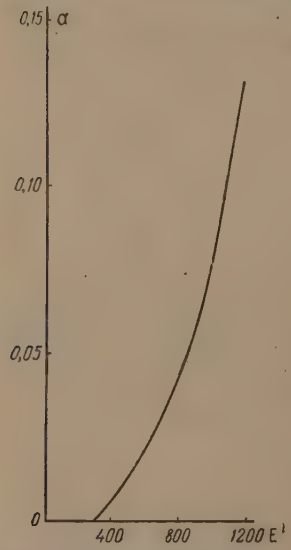

Fig. 4. The coefficient of dying out of larvae.

To solve this problem, let us determine the relation of the coefficient α to E by means of three values obtained as the result of our experiments. At E which is close to 300 V/cm, the dying out does not take place, $\alpha = 0$. At $E = 835$ V/cm $\alpha = 0.0494$, and at $E = 1110$ V/cm $\alpha = 0.113$.

We take the law of the change of α as the following function:

$$\alpha = k(E - E_0)^x.$$

Expressing E in kV and assuming that $\alpha = 0$ at $E_0 = 295$ V/cm (0.295 kV/cm) we obtain:

$$\alpha = 0.17\,(E - 0.295)^2. \qquad (2)$$

Linear relation seems to be out of the question, as there are two exact values of α and E that show:

$$\alpha = 0.231\,(E - 0.620).$$

This expression yields $\alpha = 0$ at $E = 620$ V/cm, which is at variance with the experiment. The curve of α is given in Fig. 4.

The correlation (2) shows that for the extermination of the cockchafer it is more economical to use the highest voltage. Having some quantity of available power, we may use the latter at different E and different exposures t_{exp} ($E^2 t_{exp}$ being constant). Let us use the curve II: $E = 835$ V/cm, $t_{exp} = 2$ sec.

For this curve we have found that $\alpha = 0.062$. If the power consumed during this experiment had been expended in 1 sec. instead of 2 sec., we should have taken $E = 835\sqrt{2}$, i. e. 1180 V/cm. From equation (2) we should obtain:

$$\alpha = 0.17\,(1.18 - 0.295)^2 = 0.134,$$

i. e. that the coefficient of dying out would have been much greater. This signifies in its turn that the biological effect in our experiments increases sharply with the voltage. With the same power consumption as in the second case (curve *II*), the death rate of larvae is expressed by curve IV (Fig. 2). In practical work it is very desirable (and necessary) to try to reduce the consumption of power.

It is not important during what period of time all the larvae (or nearly all) will disappear, be it one hour or 20 days, provided they perish. It being so, we should try to use as high a voltage as possible and as short an exposure as possible, so as to lessen the consumed power, provided α does not decrease below a predetermined limit. Unfortunately, we cannot speak now about an exposure less than 1 sec. Additional experiments with correctly measured exposure of less than 1 sec. are necessary.

It is interesting to note that with the increase of voltage the current increases proportionally. If at $E_1 = 835$ V/cm the current equals I_1, then at $E_2 = 1180 = 835\sqrt{2}$ it will be equal to $I_2 = I_1\sqrt{2}$. As to the total charge that passed through our system it may be said that in the second case the charge will be lower and will equal $Q = \frac{Q_1}{\sqrt{2}}$ (where Q_1 is the charge that passed in the first case). Considering that in relation to E the proportionality of all the electric values is preserved, we assume that the current, the voltage and the charge per larva change in the same relation as for the whole system; consequently, the influence exercised on the larva is due mainly to the current or the voltage and not to the charge, which decreases.

This question, as well as the influence of unstable state, which may play an important role here, must be cleared up by detailed experiments.

A. V. Lugovoj and D. C. Beklemišev have taken part in the present investigation.

Conclusions

1. The exponential law of dying out of cockchafer larvae exposed to the action of electric current (at the frequency of 50 cycles per sec.) has been found by experiment.

2. The coefficient of dying out depends upon the voltage applied to the condenser and increases rapidly with this voltage.

3. For the practical extermination of the larvae it is necessary to use as high a voltage as possible.

4. It is necessary to determine the relation of the coefficient of dying out to short exposures and very high voltages.

By the method based on the observation of the coefficient of dying out of any organism it is possible to study the factors influencing the organism when subjected to the action of electric current.

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REFERENCES

[1] A. V. Lugovoj, C. R. Acad. Sci. URSS, IV, № 7 (1936).

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PHYSIKALISCHE CHEMIE

DIE POTENTIALE VON SILBER UND EINIGEN ANDEREN METALLEN IN LÖSUNGEN VON HALOIDSALZEN

Von I. P. MORKOVKO und E. W. ZMAČINSKIJ

(Vorgelegt von S. I. Wawilow, Mitglied der Akademie, d. 19. IX. 1937)

Die Potentiale der Metalle in Fremdionenlösungen haben in letzter Zeit die Aufmerksamkeit vieler Forscher wegen der theoretischen und praktischen Bedeutung dieses Themas auf sich gezogen. In theoretischer Hinsicht ist es interessant, eine Erklärung für den Entstehungsmechanismus des Potentialsprunges im Systeme Metall—Fremdionenlösung zu geben; in praktischer Hinsicht ist es wichtig, das Verhalten der Oberfläche der Metalle zu kennen, die mit verdünnten und konzentrierten wässrigen Salzlösungen in Berührung stehen, welchen man in der Natur und der Technik begegnet—hierauf bezieht sich die Korrosion der Metalle, ihre olygodynamische Wirkung usw.

Da bezüglich dieser Frage verhältnismässig wenig experimentelles Material vorliegt ([1–7]), so untersuchten wir zur Ergänzung und nachfolgenden theoretischen Verallgemeinerung desselben eingehend die Potentialsprünge am Silber in den Haloidsalzlösungen NaCl, NH_4Cl, $BaCl_2$, $CdCl_2$ und KJ; zum Teil sind die Potentialsprünge von Ag, Cu, Pt, Au und Ni in KCl-Lösung untersucht worden.

Die Messungen haben in Übereinstimmung mit den analogen Arbeiten anderer Autoren gezeigt, dass die Potentialsprünge reproduzierbar sind, wobei die reproduzierbaren und stabilen Potentiale erst nach einem gewissen, zuweilen ziemlich langen Zeitintervall (von 1 Stunde bis zu 3 Tagen) erhalten werden; besonders ist letzteres bei der Arbeit mit konzentrierten Lösungen zu beobachten.

Wenn auch in konzentrierten Lösungen reproduzierbare Potentiale erhalten werden, so sind sie doch gegen Schütteln und Umrühren—was eine Verringerung des Potentials nach sich zieht—empfindlich. So beträgt z. B. im ruhenden Zustand im System Ag/gesättigtes NaCl der Potentialsprung +0.110 V, während er beim Umrühren auf 0.092V zurückgeht; wenn das System sich selbst überlassen bleibt, so kehrt der Potentialsprung zu dem ursprünglich gemessenen Wert zurück.

In verdünnten Lösungen besteht kein wahrnehmbarer Unterschied zwischen dem Potentialsprung im Ruhezustande und dem Potentialsprung beim Umrühren.

Der Einfluss der Verunreinigung der Elektroden mit Fett zeigte sich

darin, dass zur Erzielung eines konstanten Potentialsprunges eine längere Zeit als bei der reinen Elektrode nötig war*.

Es wurde auch der Temperatureinfluss im Intervalle von 18—50° C untersucht. Für den Temperaturkoeffizienten $\frac{dE}{dT}$ erhielten wir zur Orientierung dienende Grössen, welche für die verschiedenen Elektrolyte und Temperaturintervalle von 0.001 bis 0.00008 V pro 1° schwankten.

Bei gleichen übrigen Bedingungen sind die Hauptfaktoren, welche das Potential der betrachteten (Silber-) Elektrode bestimmen, die Natur und die Ionenkonzentration des Fremdionenelektrolyts, wobei die Konzentrationszunahme eine Verringerung des Potentialsprungs nach sich zieht. Verschiedene Kationen haben bei ein und demselben Anion jedoch nur einen geringen Einfluss auf das Potential; dieser ist durch die verschiedene Aktivität der Elektrolyte bei der gleichen Konzentration zu erklären.

Die obigen Sätze kann man durch folgende Zahlen illustrieren.

Tabelle 1

Normalität des Elektrolyts	Potential der Silberelektrode in den Salzlösungen					
	NaCl	NH_4Cl	KCl	$BaCl_2$	$CdCl_2$	KJ
0.001	0.3998	0.3683	—	0.3142	—	—
0.01	0.3368	0.3199	0.3090	0.2982	—	—0.0280
0.1	0.2890	0.2872	0.2787	—	—	—0.0836
0.5	—	0.2366	0.2279	0.2436	0.2807	—0.1446
1	0.2242	0.1833	0.2014	0.2113	0.2588	—0.1677
2	0.1893	0.1402	0.1769	—	0.2327	—0.2273
4	0.1005	0.0762	0.0785	—	0.1919	—0.3268

Selbstverständlich muss der Einfluss der Natur der Elektrode von Bedeutung sein, was auch experimentell bei der Messung der Potentialsprünge an Pt, Au, Cu und Ni in einer KCl-Lösung bestätigt wurde. Mit Verstärkung der elektropositiven Eigenschaften des Metalls nimmt auch der Potentialsprung zu. So haben z. B. in einer 0.1 norm. KCl-Lösung die Potentiale von Ni, Cu, Ag, Au und Pt folgende entsprechende Werte: —0.493; +0.089; 0.279; 0.369 und 0.405.

Der Potentialsprung am Metall in einer Fremdionenlösung kann analytisch in Form einer logarithmischen Funktion der Aktivität des Elektrolyts dargestellt werden: $E_{Me'/Me''Hl}=a+b \log cf$, und graphisch durch eine Gerade, die einen Knick beim Übergang (ungefähr zwischen 0.5 und 1.0 norm. Konzentration) von verdünnten zu konzentrierten Lösungen besitzt. Folglich sind a und b gewisse Konstanten, die jedoch für verdünnte und konzentrierte Lösungen verschieden sind (und natürlich für Lösungen mit verschiedenen Anionen). Der Knick der Geraden beim Übergange ins Gebiet konzentrierter Lösungen weist darauf hin, dass im Systeme noch andere Faktoren, ausser der Konzentration, ihre Wirkung auf das Potential zu äussern beginnen, indem sie die Gerade plötzlich ihre Richtung ändern lassen.

In der folgenden Tabelle bringen wir die Konstanten a und b für eine Silber- und eine Kupferelektrode.

* Die Messungen an einer versilberten Elektrode und an einer einfach gereinigten gaben die gleichen Resultate. Einen gewissen Unterschied erhält man nur dann bei den Messungen, wenn sie nicht in Luft, sondern in einer Stickstoffatmosphäre ausgeführt werden

Tabelle 2

Elektroden	Verdünnte Lösungen		Konzentrierte Lösungen	
	a	*b*	*a*	*b*
Ag/NaCl	+0.2230	—0.0536	+0.204	—0.1905
Ag/NH_4Cl	+0.2250	—0.0481	+0.145	—0.1887
Ag/KCl	+0.1980	—0.0606	+0.165	—0.2273
Ag/$BaCl_2$	+0.2320	—0.0323	+0.140	—0.1471
Ag/$CdCl_2$	+0.2480	—0.0324	—0.020	—0.2381
Mittelwert	+0.2250	—	—	—
Ag/KJ	—0.152	—0.0625	—0.198	—0.2564
Cu/KCl	+0.007	—0.06	—0.033	—0.136
Cu/KCl*	+0.005	—0.058	—0.035	—0.141
Cu/NaCl*	+0.005	—0.058	—0.005	—0.138
Cu/KBr*	—0.088	—0.053	—0.087	—0.115

Aus einem Vergleich der Zahlenangaben in der Tabelle für die verdünnten Lösungen, können wir folgende Gesetzmässigkeiten ableiten.

1. Die Konstante *a* hat ungefähr den gleichen Wert für jedes System vom Type *Me'/Me''Hl*, wenn sich *Hl* und *Me'* nicht verändern, aber bei Änderung des Elektrolytanions und des Elektrodenmaterials ändert sich auch *a*. So hat für Silber in Chloridlösungen die Konstante *a* im Mittel den Wert +0.2250 während sie für Ag/I—0.152 beträgt.

2. Die Konstante *b* ist für beliebige Systeme vom Type *Me'/Me''Hl* (wo *Me'* =Ag, Cu) gleich gross und ändert sich nur in Abhängigkeit von der Wertigkeit des Kations. Für verdünnte einwertige Elektrolyte hat sie den Wert —0.0568; d. h. sie kann ausgedrückt werden durch $\frac{RT}{nF}$.

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ZITIERTE LITERATUR

[1] McAulay, White, Spooner, Nature, **126,** 914 (1930). [2] Schmid, Winkelmann, Helv. chim. Acta, **13,** 304 (1930). [3] Schmid, Winkelmann, Vögele, Helv. chim. Acta, **15,** 1393 (1932); **16,** 20, 22, 398 (1933). [4] Schmid, Vögele, Helv. chim. Acta, **16,** 366 (1933). [5] Есин, Лоцманова, ЖОХ, **4,** 1138 (1934). [6] Есин, Беклемишева, ЖОХ, **4,** 1394 (1934). [7] Obručeva, Frumkin, C. R. Acad. Sci. URSS, IV, 1 (1936).

ZUR THEORIE DER ENTSTEHUNG DES POTENTIALSPRUNGES AN EINIGEN METALLEN IN FREMDIONENLÖSUNGEN

Von I. P. MORKOVKO und E. W. ZMAČINSKIJ

(Vorgelegt von S. I. Wawilow, Mitglied der Akademie, d. 19. IX. 1937)

In der vorhergehenden Arbeit untersuchten wir eine Reihe von Systemen mit Silber- und Kupferelektroden in Haloidsalzen, gaben wir eine allgemeine Charakteristik der Potentiale in diesen Systemen, zählten die Faktoren auf, die von Einfluss auf das Potential sind, und ermittelten die funktionelle Abhängigkeit zwischen dieser Grösse und der Aktivität der Fremd-

* Die Konstanten *a* und *b* sind auf Grund der Messungen von Schmid (2) berechnet worden.

ionenlösung in Gestalt der Gleichung $E=a+b \log cf$, ebenso hoben wir die Gesetzmässigkeiten in den Werten der Konstanten a und b hervor.

Bei der Betrachtung unserer Systeme (Silber in Haloidsalzlösungen) wie auch der von Schmid (1) (Kupfer in Alkalimetallsalzlösungen) und Jessin (2) (Gold und Silber in Silber- und Kupfersalzlösungen) untersuchten Systeme, können wir dieselben in zwei Klassen einteilen. In der einen Klasse steht das Potential in Abhängigkeit von der Anionenaktivität (wobei mit der Konzentrationszunahme des Elektrolyts das Potential absinkt), und in der anderen—von der Kationenaktivität (wobei mit der Konzentrationszunahme des Elektrolyts das Potential ansteigt).

Einige Autoren (Jessin u. a.) schlagen eine Theorie vor, die die Entstehung des Potentialsprungs in den Systemen beider Klassen vorzugsweise auf die Adsorption der Anionen oder Kationen zurückführt.

Wir sind jedoch auf Grund der weiter unten dargelegten Tatsachen und Überlegungen der Meinung, dass die Ursache für die Entstehung des Potentialsprunges in Gegenwart von Fremdionenlösungen in der chemischen Wechselwirkung zwischen Elektrode und Elektrolyt zu suchen ist.

1. Für die Systeme $Me'/Me''Hl$ (unsere und die von Schmid, wo Me' =Ag, Cu) besteht diese Wechselwirkung in der Auflösung des Metalls in dem Haloidsalz, was zur Bildung von Elektroden zweiter Art vom Type $Ag/AgCl/Cl'$ führt.

Wir haben experimentell die Löslichkeit von Silber und Kupfer in Haloidsalzlösungen gezeigt. So ergibt Silber bei der Auflösung in gesättigter KCl-Lösung AgCl, das in ein komplexes Salz übergeht. Die Lösung dieses Salzes 1) wird durch Wasser zersetzt und ergibt eine weisse AgCl-Trübung, 2) gibt einen Niederschlag mit KJ (gelb) und H_2S (schwarz). Die Löslichkeit von Kupfer in KCl wird durch die Reaktion mit Ammoniak nachgewiesen (bläuliche Färbung).

Den Lösungschemismus von Silber bzw. Kupfer kann man sich folgendermassen vorstellen. Das Haloidsalz in der Lösung wird teilweise hydrolisiert, wobei es eine Haloidwasserstoffsäure produziert, welche das Metall unter Bildung dessen Halids löst.

Aus diesem Grunde treffen bei uns alle Bedingungen zu, die zur Bildung einer Ellektrode zweiter Art notwendig sind.

Da das Potential der Elektrode zweiter Art durch die Formel

$$E_{Ag/AgCl/Cl'} = E_{Ag/AgCl/nCl'} - \frac{RT}{nF} \log C_{Cl'}$$

ausgedrückt wird, so müssen wir, durch Vergleich derselben mit der von uns gegebenen Formel $E=a+b \log cf$, haben:

1) eine Übereinstimmung der Konstanten a mit dem Potential der Elektrode zweiter Art bei normaler Cl'-Ionenkonzentration,

2) eine Übereinstimmung der Konstanten b mit der Konstanten $\frac{RT}{nF}$ (die für 291° gleich 0.058 ist) und, eo ipso,

3) eine Übereinstimmung der Potentiale in den untersuchten Systemen mit den entsprechenden Potentialen zweiter Art, die sowohl aus dem Löslichkeitsprodukt berechnet, wie auch experimentell bestimmt wurden.

Als Illustration zum ersten Punkt kann die Tabelle 1 dienen.

Die Übereinstimmung ist, wie zu sehen, sehr befriedigend.

Was die Konstante b anbetrifft, so liegt sie, wie wir in der vorhergehenden Arbeit gezeigt haben, in der Nähe von 0.058.

Zum Vergleiche der Potentiale bringen wir die experimentell und aus der Formel: $E_{Ag/AgCl/Cl'}=0.2245-0.058 \log C_{Cl'}$ berechneten Werte (Tab. 2).

Tabelle 1

Konstante a	$E_{Ag/Me\,Hl'}$ experim. gefunden	$E_{Ag/AgHl/nHl'}$ aus dem Löslichkeitsprodukt berechnet	$E_{Ag;AgHl/nHl'}$ nach Angaben anderer Autoren*
0.2250	Ag/nNaCl 0.2242	Ag/AgCl/1 nCl' 0.2307	Ag/AgCl/nCl' 0.2245
—0.152	Ag/nKJ —0.167	Ag/AgJ/nJ' —0.130	Ag/AgJ/nJ' —0.14

Für verdünnte Lösungen unterscheiden sich die gefundenen Werte von den berechneten nur wenig.

Tabelle 2

Normalität des Elektrolyts	$E_{Ag/NaCl}$ gefunden	$E_{Ag/AgCl/Cl'}$ berechnet	Differenz
0.001	0.3998	0.3995	+0.0003
0.01	0.3368	0.3432	—0.0064
0.1	0.2890	0.2890	±0.0000
1	0.2242	0.2352	—0.0110
2	0.1893	0.2174	—0.0283
4	0.1005	0.1959	—0.0954

Vom Standpunkte der dargelegten Theorie der chemischen Wechselwirkung zwischen Elektrode und Elektrolyt sind alle Erscheinungen leicht zu erklären, die bei der Untersuchung der Potentiale an einer Silber- und Kupferelektrode in Fremdionenlösungen beobachtet wurden.

a) Die langdauernde Einstellung des Potentialsprungs am Metall ist dadurch zu erklären, dass die Auflösung des Metalls, bevor eine gesättigte Lösung des Metallsalzes erhalten wird—und wenn auch nur in der Umgebung der Elektrode,—eine lange Zeit erfordert.

b) Der Einfluss des Umrührens kann damit erklärt werden, dass dadurch eine Konzentrationsverringerung der Metallionen in der Nähe der Elektrode hervorgerufen wird und dies eine Potentialabnahme mit sich bringt.

c) Eine Verunreinigung der Elektrode mit Fett verhindert die Auflösung des Metalls und verzögert die Einstellung des Potentials.

d) Daraus, dass das Potential der Elektroden zweiter Art durch die Anionenkonzentration des Fremdionenelektrolyts bestimmt wird, geht hervor, dass dessen Kation keinen Einfluss auf das Potential haben darf. Der scheinbare Einfluss des Kations wird durch die verschiedene Aktivität der Elektrolyte bei der gleichen Konzentration erklärt.

e) Der Kurvenknick, der die Abhängigkeit des Potentials von der Konzentration c (oder der Aktivität cf) beim Übergange von verdünnten zu konzentrierten Lösungen des Elektrolyts zum Ausdruck bringt, ist zum Teil durch die Bildung des Komplexsalzes des Metalls zu erklären.

II. Für Systeme, in denen das Potential von der Natur des Kations abhängt, d. h. in Systemen, wie sie von Jessin untersucht worden sind (Edelmetall in einem Salz eines weniger edlen Metalls, z. B. Au in $AgNO_3$, oder Ag in $CuSO_4$), besteht die chemische Wechselwirkung zwischen Elektrode und Elektrolyt in der Ausscheidung des Elektrolytkations auf der Elektrode in metallischer Form und in der Auflösung der Elektrode, z. B. $2\,AG+ +Cu^{\cdot\cdot}=Cu+2Ag^{\cdot}$**.

* Siehe Lewis u. Randall, Chemische Thermodynamik, S. 336 (1936); Britton, Wasserstoffionen, S. 36 (1936); Klassen, Elektroanalyse, L.—B., T. II. 1027 (1934).

** Die Kupferausscheidung ist an dem gelben Anfluge auf einer Silberplatte zu merken, die einige Tage in einer gesättigten $CuSO_4$-Lösung gestanden hat; die Kontrolplatten in einer KCl-Lösung und in Luft behielten ihren weissen Silberglanz. Die Ausscheidung eines weniger edlen Metalles auf einem edleren wurde von Obrutschewa und Frumkin [3] beobachtet, welche einen kristallischen Silberniederschlag auf Platin erhielten,

Als Resultat bildet sich eine gemischte Elektrode (erster Art) aus zwei Metallen oder ein doppeltes galvanisches System. Solche Systeme wurden von Akimov und Tomašev [4] untersucht. Sie fanden, dass das Potential eines solchen Systems einen Zwischenwert zwischen den Potentialen beider Metalle besitzt. Dies trifft auch bezüglich der von uns betrachteten Systeme zu.

Als Beweis führen wir folgenden Versuch an. Wir haben das Silberpotential in einem Kupfersalz (Ag/gesättigt. $CuSO_4$=0.522 V) gemessen und verglichen es mit dem Silberpotential in einem Silbersalz (Ag/gesättigt. Ag/SO_4=0.735 V) und dem Kupferpotential in einem Kupfersalz (Cu/gesättigt. $CuSO_4$=0.330 V). Es hat sich gezeigt, dass das Potential Ag/gesättigt. $CuSO_4$ wirklich einen Zwischenwert zwischen den beiden letzteren obenangeführten Potentialen annimmt, und ungefähr mit ihrem arithmetischen Mittelwert $\frac{0.735 + 0.330}{2} = 0.533$ V übereinstimmt.

Dieser Umstand berechtigt uns zu der Annahme, dass das ursprüngliche System Ag/Cu·· sich in das sekundäre System Ag, Cu/Ag·Cu·· verwandelt.

Zur Bekräftigung bringen wir hierfür noch Berechnungen auf Grund der aus den Arbeiten von Jessin und Mitarbeitern entlehnten Angaben an; sie sind in der nachfolgenden Tabelle zusammengestellt.

Tabelle 3

Normalität des Elektrolyts	$E_{Cu/Cu(NO_3)_2}$	$E_{Ag/AgNO_3}$	Arithmetischer Mittelwert $E_{Cu/Cu^{··}} + E_{Ag/Ag^{·}}$	Gefunden $E_{Ag/Cu(NO_3)_2}$	Differenz
7	0.4298	0.824	0.6269	0.5609	0.0860
5	0.4082	0.819	0.6136	0.5312	0.0824
3	0.3820	0.810	0.5960	0.5127	0.0833
2	0.3658	0.803	0.5844	0.5060	0.0784
1.5	0.3569	0.799	0.5729	0.4934	0.0795
1.0	0.3468	0.792	0.5694	0.4868	0.0826
0.75	0.3402	0.787	0.5636	0.4800	0.0836
0.5	0.3331	0.779	0.5560	0.4770	0.0790
0.0125	0.3079	0.708	0.5079	0.4365	0.0714
0.00125	0.2979	0.665	0.4813	0.4240	0.0673
				Mittelwert	0.0793

Aus der Tabelle ist ersichtlich, dass die von uns überschlagsmässig berechneten Grössen für das Potential $Ag/Cu(NO_3)_2$ sich wenig von den gefundenen unterscheiden, indem sie die letzteren um eine geringe, aber konstante Grösse übertreffen, die ungefähr 0.08 ausmacht.

Eine Beziehung dieser Art ist nicht zufällig—sie drückt eine Gesetzmässigkeit aus, die durch die Natur der Metallelektrode und des Elektrolyts und die zwischen ihnen stattfindende chemische Wechselwirkung bedingt wird.

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ZITIERTE LITERATUR

[1] A. Schmid, W. Winkelmann, Helv. chim. Acta, 13, 304 (1930). [2] Есин и сотрудники, ЖОХ, 4, 1138 (1934); 4, 1394 (1934). [3] Obručeva, Frumkin, C. R. Acad. Sci. URSS, IV (XIII), 1 (1936). [4] Акимов, Томашев, ЖФХ, 8, 623 (1936).

welches sich in einer $AgNO_3$-Lösung befand. Die Autoren erklären die Silberausscheidung durch die Existenz des Ag-Ions in der Lösung, welches beim Zerfall metallisches Silber abspaltet. In unserem Falle ist es schwierig, eine solche Analogie durchzuführen, da das Cu··-Ion unbekannt ist.

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BIOCHIMIE

ACTION DES MÉTAUX ALCALINS SUR LE COLLAGÈNE

Par I. A. SMORODINZEV et S. A. PAVLOV

(Présenté par A. A. Richter, de l'Académie, le 2. X. 1937)

Ayant prouvé l'absence de l'hydrolyse du collagène dans le cas de sa macération prolongée (100 jours) avec des sels neutres (1), nous sommes passés à l'étude du dynamisme de ce processus dans le temps et nous avons choisi comme indice la détermination du coefficient *D*.

Le collagène (poudre commerciale de déchets de peau) était mis dans des flacons et recouvert de solutions de chlorure de sodium ou de sulfate de sodium (0.5 mol.) dans la proportion de 1 : 20, puis il était mis à macérer à la température de 17—19°; à des intervalles de temps déterminés, indiqués dans les tableaux, nous prélevions des portions de liquide de 25 ml, en nous servant chaque fois de flacons particuliers, et nous déterminions le coefficient *D* selon la méthode habituelle, au moyen de l'hydrate colloïdal d'oxyde de fer (2). Les résultats des observations sont donnés dans les tableaux 1—4.

Tableau 1

Solution de chlorure de sodium (0.5 mol.)

Termes de prise des échantillons	2 h.	2 j.	5 j.	8 j.	11 j.	14 j.	17 j.	20 j.
E en ml	0.42	0.23	0.48	0.40	0.41	0.33	0.55	0.75
F » »	0.60	0.33	0.56	0.56	0.77	0.73	1.26	1.52
Coefficient *D*	1.36	0.73	0.59	1.25	2.64	2.93	5.21	5.65

Le tableau 1 montre que l'acidité totale de l'extrait (*E*) diminue de moitié vers le 2-me jour, puis elle augmente et se maintient environ au même niveau pendant 2 semaines; ensuite elle augmente progressivement jusqu'à son double. Cette marche de la modification de la valeur *E* indique une liaison des valences acides dans les premiers jours de macération avec les sels et leur dégagement à la troisième semaine.

La marche de la modification de la valeur *F* («acidité alcoolique») indique que, sous l'influence de la macération avec les sels, il se produit également vers le 2-me jour une forte liaison des groupes carboxylés; vers le 5-me jour ils reviennent au niveau initial et à partir du 11-me jour jusqu'à

la fin, on observe une augmentation progressive de l'acidité titrable à l'alcool, aux dépens de l'énolisation des liaisons peptidiques (1). En résultat de ces modifications des composants E et F, le coefficient D diminue presque de moitié vers le 2-me jour; cette diminution continue jusqu'au 5-me jour; au 8-me jour le coefficient D revient au niveau initial et s'élève fortement dans la suite.

L'expérience effectuée avec la solution de chlorure de sodium (0.5 mol.) a été répétée avec une autre préparation de collagène.

Tableau 2

Solution de chlorure de sodium (0.5 mol.)

Termes de prise des échantillons . .	2 j.	5 j.	8 j.	12 j.	15 j.	18 j.	24 j.
E en ml	0.52	0.10	0.15	0.24	0.28	0.20	0.22
F » »	0.72	0.20	0.40	0.88	1.05	0.82	0.79
Coefficient D	1.44	0.72	1.95	4.61	5.54	4.46	4.11

Dans cette expérience (tableau 2) la valeur E atteint son minimum non pas au 2-me, mais au 5-me jour et se maintient ensuite à un niveau abaissé, ce qui indique la liaison des valences acides du collagène dans le processus de sa macération avec le sel neutre. Le blocage des groupes carboxylés augmente également au début et le minimum de la valeur F («acidité alcoolique») coïncide avec le 5-me jour aussi, tandis que le maximum d'énolisation des groupes peptidiques coïncide avec le 15-me jour. Vers le 5-me jour le coefficient D diminue; une forte augmentation commence à partir du 12-me jour, elle atteint son maximum le 15-me jour et diminue légèrement ensuite. Malgré la grande différence existant entre les chiffres absolus des expériences, indiquées aux tableaux 1 et 2, la tendance générale du processus reste la même.

Des expériences analogues ont été faites avec une solution de sulfate de sodium (0.5 mol.).

Tableau 3

Solution de sulfate de sodium (0.5 mol.)

Termes de prise des échantillons	2 h.	2 j.	5 j.	8 j.	11 j.	14 j.	17 j.	20 j.
E en ml	0.30	0.28	0.30	0.16	0.35	0.25	0.40	0.29
F » »	0.35	0.46	0.37	0.18	0.38	0.59	0.77	0.75
Coefficient D	0.44	0.36	0.25	0.12	0.22	2.56	2.71	3.30

Sans compter le 8-me jour, où l'acidité a diminué de moitié pour telle ou autre raison, la valeur E reste presque invariable. Dans le cas de macération du collagène avec une solution de sulfate de sodium (0.5 mol.), le dégagement des valences acides n'a pas lieu, probablement parce que le coefficient de dissociation de l'acide sulfurique est inférieur à celui de l'acide chlorhydrique. C'est probablement pour la même raison que les chiffres

absolus de la valeur E sont moins élevés dans le cas d'emploi du sulfate de sodium que dans le cas d'emploi du chlorure de sodium. La valeur F reste aussi au même niveau jusqu'au 11-me jour (excepté le 8-me jour) et augmente ensuite presque du double.

Conformément à ces modifications, le coefficient D, après avoir baissé au début, se maintient au même niveau jusqu'au 11-me jour et s'élève brusquement ensuite.

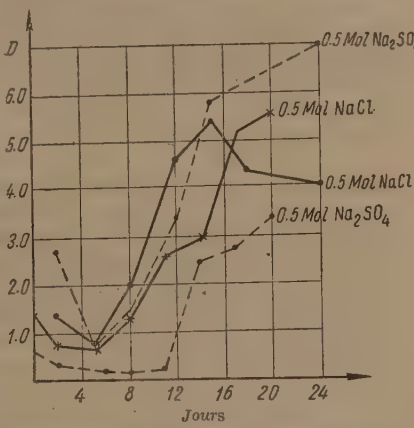
L'expérience faite avec une solution de sulfate de sodium a aussi été répétée avec une autre préparation de collagène.

Tableau 4

Solution de sulfate de sodium (0.5 mol.)

Termes de prise des échantillons . .	2 j.	5 j.	8 j.	12 j.	15 j.	18 j.	24 j.
E en ml	0.14	0.14	(0.31)	0.14	0.19	0.26	0.15
F » »	0.52	0.25	0.51	0.61	1.00	1.00	1.13
Coefficient D	2.74	0.79	1.44	3.38	5.83	5.33	7.06

Dans cette expérience (tableau 4) la valeur E ne varie pas au cours de 12 jours (exceptant de nouveau le 8-me jour!). La valeur F («acidité alcoolique»), après avoir baissé au 5-me jour, se maintient environ au même niveau jusqu'au 12-me jour, puis elle augmente du double. Vers le 5-me jour, le coefficient D diminue fortement, s'égalise vers le 12-me jour, puis augmente brusquement. Dans les expériences indiquées dans les tableaux 3 et 4, on observe une différence considérable en ce qui concerne les chiffres absolus, ce qui dépend de la qualité des préparations de collagène, mais la marche du processus est la même dans les deux cas (figure).



Modification du coefficient D dépendant de la durée du traitement de collagène par des solutions de 0.5 mol de NaCl et de Na_2SO_4.

En comparant les quatre tableaux dans lesquels sont donnés les chiffres typiques d'une série d'expériences, nous ne trouvons pas de grande différence dans l'action de ces deux sels sur les composants du coefficient D et sur le coefficient même. Presque dans tous les cas, on observe d'abord une diminution des valeurs E, F et D, puis une égalisation, qui donne toujours place, à la fin de l'expérience, à une élévation considérable. Ce fait peut facilement être expliqué sous l'aspect de nos idées théoriques sur les combinaisons chimiques des composants des sels avec les groupes actifs de protéine et sur l'énolisation des liaisons peptidiques de protéine dans le cas de macération prolongée avec des sels. Le processus de cette combinaison s'effectue lentement et n'est clairement apparent qu'au bout de 2—3 semaines de macération avec le sel. La modification de la valeur F nous permet de juger du comportement des groupes aminés dans le cas de l'action des sels neutres sur les protéines, vu que l'addition d'alcool écarte le blocage des

carboxyles par les groupes aminés. L'analyse détaillée du coefficient D et de ses composants permet de suivre le dynamisme de ce processus dans les différentes phases de son développement.

Conclusions

1. L'étude des modifications du coefficient D dans les extraits aux sels du collagène confirme notre théorie sur la combinaison chimique des sels neutres avec les groupes actifs de protéine.

2. Au début de la macération du collagène avec le sel, on a observé dans tous les cas une diminution de l'acidité totale (E) et des carboxyles bloqués par les groupes aminés (F «acidité alcoolique»), en résultat de la combinaison de la protéine avec le sel.

3. Après une macération de 2 à 3 semaines, la valeur E, et surtout la valeur F, augmentent toujours fortement. Par conséquent, une grande quantité de groupes actifs de protéine entre peu à peu en combinaison avec le sel et augmente progressivement l'énolisation des liaisons peptidiques.

4. On ne remarque pas de différence particulière dans l'action du chlorure et du sulfate de sodium sur le collagène, en ce qui concerne la modification du coefficient D.

5. La valeur absolue du coefficient D et de ses composants varie selon les propriétés de la poudre de déchets de peau, qui ne représente pas un individu chimique.

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le 2. X. 1937.

LITTÉRATURE CITÉE

[1] I. A. Smorodinzev et S. A. Pavlov, Bull. Soc. chim. biol., **19**, 915 (1937). [2] I. A. Smorodinzev et S. A. Pavlov, C. R. Acad. Sci. URSS, XV, 479 (1937).

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PLANT PHYSIOLOGY

MAGNESIUM AS AN ACTIVATOR OF BIOCHEMICAL CONVERSIONS

By V. S. BUTKEVIČ (BUTKEWITSCH), Corresponding Member of the Academy, and E. I. TROFIMOVA

The effect of mineral salts on plants has been the subject of numerous investigations but the importance of the different mineral elements in biochemical conversions still remains but little known. This is particularly true of salt cations, including magnesium.

Magnesium plays an important role in plant life, inasmuch as it enters into the composition of chlorophyll. But, as is well known, its role is not ristricted to this. Magnesium is an essential constituent of all plasmic formations, including those not containing chlorophyll. There are reason to believe that the significance of magnesium in the photosynthetic process is not merely that of a constituent of chlorophyll (1). The active participation of magnesium in the conversion of plant substances shown by its being contained in the organs where food materials are store as well as in young organs (2), and by its transport, when the plant is insufficiently supplied with it, from the old leaves to the young ones (3).

The role of magnesium, the same as that of potassium, is usually associated with the conversion of carbohydrates in plants (4).

After Loman's data, confirmed by Eyler and Nielson, magnesium enters into the cozymase system as a sugar-activating element (5). Our experiments, carried out in cooperation with Timofejeva, have shown that magnesium greatly activates the production and accumulation of citric acid in cultures of *Aspergillus niger* on sugar. On lowering the magnesium content till it becomes a factor limiting the growth of the fungus, the accumulation of citric acid drops almost to zero (6).

Below are reported the results of experiments on the influence of magnesium salts upon the accumulation of citric and oxylic acids by mycelia in acetate solutions with and without the addition of sugar (7).

Experiment 1. The mycelia of *Aspergillus niger* (Strain 1a) were grown for 48 hours at 32° in the ellipsoidal flasks, usually employed by us, on the usual nutrient solution with 5% of sugar. The nutrient solution was then removed and the mycelia were kept for 24 hours at the same temperature in equivalent solutions of sodium and magnesium sulphates ($Na_2SO_4 \cdot 10H_2O$, 2.5%; $MgSO_4 \cdot 7H_2O$, 2.37%). After that they were transported to a solution of sodium acetate (2.5% of acetic acid), both with and without the addition of 1% of sugar, and to a 10% sugar solution without the acetate. When substituting the salt solutions for the nutrient solution, the mycelia were thoroughly rinsed in a 2.5% solution of sodium sulphate. On removing the salt solutions, the experimental solutions were

introduced under the mycelia without any preliminary washing. The mycelia remained on these solutions for one and three days at 32°. At the end of that time, the solutions were analysed. The results of these analyses are summarized in Table 1. The figures of that table are the mean of two

Table 1

Composition of experimental solution	Mycelia kept on salt solution	Duration of experiment in days	Acetic acid grams	Sugar grams	Citric acid grams	Citric acid yield from sugar %	Oxalic acid grams	Acidity of experimental solution 0.1 *n* NaOH per 10 cm³ cm³	Weight of mycelium, grams
Sodium acetate (2.5% acetic acid)	Na_2SO_4	1	1.138	—	0	—	0.710	Alkaline	0.80
		3	0	—	0	—	1.732	Weakly acid	0.61
	$MgSO_4$	1	0.317	—	Traces	—	1.416	1.0	0.88
		3	0	—	0	—	1.794	2.1	0.65
Sodium acetate (2.5% acetic acid) + 1% sugar	Na_2SO_4	1	1.525	0.330	0.053	8	0.403	Weakly acid	0.94
		3	0.726	0.052	0.124	—	1.018	»	0.87
	$MgSO_4$	1	0.183	0.173	0.389	47	1.057	2.5	1.14
		3	0	0.016	0	—	1.938	4.7	1.04
10% Sugar	Na_2SO_4	1	—	7.180	0.440	—	0.249	12.4	1.90
		3	—	4.643	1.010	19	0.515	27.1	1.99
	$MgSO_4$	1	—	6.470	0.969	—	0.242	20.2	1.75
		3	—	5.678	1.600	37	0.400	33.8	1.85

parallel experiments. The control mycelia kept on solutions of sodium and magnesium salts showed a mean dry weight of 1.02 and 1.07 g respectively. After three hours boiling with 2% hydrochloric acid, they yielded 48 and 75 mg of substances reducing Fehling solution respectively, as calculated from the amount of glucose.

The above data show that keeping the mycelia of the magnesium salt increased their activity considerably, both as regards the production of citric acid and the conversion of acetic into oxalic acid. The magnesium also raised the yield of citric acid from sugar. The following experiment gave analogous results.

Experiment 2. Made in the same manner as the firts experiment with the only difference that the mycelia were 2.5 days old and that the mycelia kept on the solution of magnesium salt were compared with those taken directly from the nutrient medium without keeping them on the solution of sodium sulphate. The whole experiment continued two days. The results the mean of two parallel experiments are summarized in Table 2.

In this experiment, as in the preceeding one, we observed (in addition to the above-noted effect of the magnesium on the production of citric and oxalic acids) a considerable increase in the total acidity determinable by titration which is not accounted for by the acids determined during the analysis.

The control mycelia, both those kept on the magnesium salt and those not kept on it, had a dry weight of 1.37 and 1.35 g. After boiling with 2%

Table 2

Composition of experimental solution	Mycelia kept on salt solution	Duration of experiment in days	Acetic acid grams	Sugar grams	Citric acid grams	Citric acid yield from sugar %	Oxalic acid grams	Acidity of experimental solution. 0.1 *n* NaOH per 10 cm³ cm³	Weight of mycelium, grams
Sodium acetate (2.5% acetic acid)	—	1	1.611	—	0	—	0.440	Alkaline	1·03
		2	0.875	—	0	—	0.995	»	0.93
	$MgSO_4$	1	0.735	—	0.061	—	0.960	0.7	1.12
		2	0	—	0	—	2.195	7.4	1.07
Sodium acetate (2.5% acetic acid) +1% of sugar	—	1	1.757	0.495	0.120	24	0.307	Weakly acid	1.13
		2	1.342	0.208	0.170	—	0.574	»	1.05
	$MgSO_4$	1	0.449	0.476	0.420	80	1.023	2.0	1.40
		2	0	0.080	0.235	—	2.218	16.5	1.40
1% sugar	—	1	—	0.325	0	—	0.097	2.1	1.56
		2	—	0.138	0	—	0.126	2.9	1.50
	$MgSO_4$	1	—	0.368	0	—	0.128	3.0	1.45
		2	—	0.192	0	—	0.166	3.7	1.45

hydrochloric acid, they yielded 38 and 88 mg of reducing substances respectively. This experiment has thus also shown that the mycelia kept on the solution of magnesium salt contain a higher quantity of substances yielding reducing products on acid hydrolysis. A third experiment was made to check up the result obtained from the two preceeding experiments.

Experiment 3. Eight mycelia grown under the same conditions as in experiment 2, were taken in this experiment. Four of them were examined directly from the nutrient medium, while the other four were examined after having been kept for 24 hours on a solution of magnesium sulphate. The results obtained are summarized in Table 3.

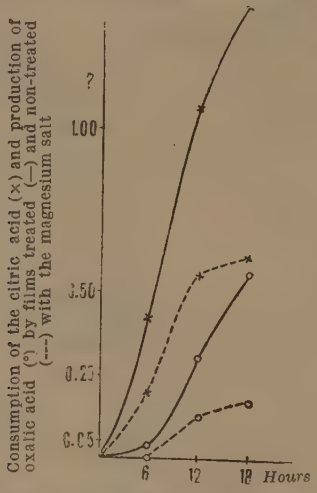
Table 3

Mycelium No	Treatment of mycelia	Weight of mycelia grams	Content of reducing substances in mycelia referred to glucose mg
1	Untreated directly from the nutrient medium	1.34	35
2		1.39	41
3		1.39	41
4		1.44	37
		1.39	38
5	Kept for 24 hours on a solution of $MgSO_4$	1.33	82
6		1.37	72
7		1.34	101
8		1.40	80
		1.36	84

The tabulated data show a marked rise in the proportion of substances yielding reducing products on hydrolysis in all the mycelia treated with magnesium salt. It is not yet clear whether this phenomenon is in any way associated with the activation of the mycelia by that same salt.

In the next experiment, the conversion of the acetate and the sugar under the action of the solution of magnesium salt on the mycelium was traced in greater detail.

Experiment 4. The plan of this experiment was the same as that of experiment 2, with the following modifications: the mycelia were kept



on the solution of magnesium salt for 12 hours only, the experiment was carried out at 30°, and it continued in all for 18 hours, the experimental solutions together with the mycelia being taken every 6 hours for analysis. The mean results of two parallel experiments are summarized in Table 4 and partly in the figure.

Table 4

Composition of experimental solution	Mycelia kept on salt solution	Duration of experiment hours	Acetic acid grams	Sugar grams	Citric acid grams	Oxalic acid grams	Acidity of experimental solution. 0.1 *n* NaOH per 10 cm³ cm³	Weight of mycelium, grams
Sodium acetate (2.5% acetic acid)	—	6	2.295	—	0	0	Alkaline	1.08
		12	1.939	—	0	0.134	»	1.08
		18	1.908	—	Traces	0.159	»	1.09
	$MgSO_4$	6	2.059	—	0	0.033	»	1.20
		12	1.484	—	0	0.308	»	1.18
		18	1.156	—	0	0.556	»	1.19
Sodium acetate (2.5% acetic acid) +1% of sugar	—	6	2.310	0.820	0	Traces	Alkaline	1.23
		12	1.939	—	0.076	0.093	»	1.30
		18	1.817	0.582	Traces	0.186	»	1.15
	$MgSO_4$	6	2.120	0.743	0	0	»	1.22
		12	1.590	0.621	0.119	0.181	»	1.29
		18	1.301	0.586	0.127	0.378	Weakly acid	1.23
5% sugar	—	6	—	4.231	0	0.050	1.0	1.23
		18	—	3.787	0.101	0.259	8.7	1.65
	$MgSO_4$	6	—	4.146	0.084	0.078	3.0	1.30
		18	—	3.428	0.172	0.373	10.9	1.42

The control mycelia, both untreated and treated with the solution of magnesium salt, had a dry weight of 1.23 and 1.20 g respectively. After treatment with hydrochloric acid, they yielded 32 and 60 mg of reducing substances respectively. We thus find here likewise an increase in the content of these substances under the influence of magnesium salt.

The above described experiments definitely establish, in accordance with our former data on the conversion of sugar into citric acid, the activating effect of magnesium salt on certain biochemical processes of metabolism. This activation was manifested not only in the conversion of sugar into citric acid, but also in the conversion of acetic acid into oxalic acid. The question naturally arises whether the activating effect of magnesium on certain metabolic processes established in our experiments is in any way associated with the stimulating effect of magnesium on the development of plant from seeds as observed by Popov ([8]) and other investigators ([9], [10]) who worked on these problems. As is well known, magnesium salts are a usual constituent of the solutions recommended by Popov for the treatment of seeds as the most active stimulants. Investigations of the effect of magnesium on metabolism in the higher plants would be most desirable.

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REFERENCES

[1] Fleischer, Journ. Gen. Physiol., **18,** 573 (1935). [2] Dix u. Bischoff, ZS. Pfl., Dg. u. B-kde, A **18,** 158 (1930). [3] Garner a. collab., Journ. Agric. Res., **40,** 2 (1930). [4] Popp, Landw. Vers. St., **124,** 129 (1936). [5] Harden, Alcoholic Fermentation, 87 (1932). [6] Буткевич и Тимофеева, Микробиология, **3,** 574 (1934); **4,** 489 (1935); Bioch. ZS., **275,** 405 (1935). [7] Буткевич, Меншикская и Трофимова, Микробиология, **3,** 319, 554 (1934); Bioch. ZS., **272,** 290, 364 (1934); **276,** 446 (1935). [8] Popoff, Die Zellstimulation, 183 (1931). [9] Рихтер и Страхов, Ж. оп. агр. ю.-в., **5,** вып. 1 (1927). [10] Самохвалов, Химиз. соц. земл., № 4, 77 (1936).

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PLANT PHYSIOLOGY

ON THE ESSENCE OF THE PHYSIOLOGICAL ANTAGONISM OF IONS AND OF THE TOXIC PROPERTIES OF PURE NUTRIENT SALTS

By A. A. DROBKOV

(Communicated by D. N. Prianishnikov, Member of the Academy, 16. VIII. 1937)

The physiological antagonism of ions and the toxic effect of pure salts were first observed by Ringer in 1883, who noted the fact that the heart of vertebrates (frogs) quickly ceases to beat in a pure solution of sodium chloride, unless other salts are present therein.

In 1898 Loeb recorded an analogous phenomenon in marine animals. He found in his experiments that marine animals (*Fundulus*) rapidly perish in a pure solution of sodium chloride of the same concentration as that of sea water. It is, however, enough to add to that solution small amounts of other salts, such as calcium chloride or magnesium chloride,—to obtain a normal medium for their development.

From his experiments Loeb drew the conclusion that the pure salts of sodium chloride are poisonous to marine animals. This conception was later enlarged in the sense that all nutrient salts came to be considered toxic when administered singly. But when the solution contains several nutrient salts, then the toxic properties of the ones are neutralized or balanced by those of the others, thus permitting of the normal development of vegetable and animal organisms. Such solutions have been termed equilibrated solutions.

It must be noted, however, that notwithstanding the vast literature available to the subject, the essence of the physiological antagonism of salts still remains obscure and inexplicable.

In this problem, the thesis that pure nutrient salts are poisonous for plants when given singly, is especially questionable and unproved. Moreover, it is in contradiction with the existing experimental data.

Already in 1891 P. Slezkin ([1], [2]) succeeded in bringing plants in water cultures up to their 5th and 6th leaf, with the various nutrient salts being administered singly in test-tubes. Later, I. S. Shulov ([3]) working in the laboratory of Academician D. N. Prianishnikov, developed a special technique of isolate feeding, which made it possible to solve a number of important physiological problems.

Much, however, still remains obscure. The main thing was that all attempts to obtain a normal development of plants failed when not only one but all the nutrient salts of Hellrigel's mixture were administered singly.

For the purpose of studying this question I carried out in 1935 some experiments after the following scheme: four flat-sided glass vessels were stood

with their sides touching. Some distilled water was poured into each vessel and Hellrigel's mixture was introduced as follows: into one vessel was added $Ca(NO_3)_2$, into the second KH_2PO_4+KCl, into the third $MgSO_4$, while iron citrate plus the microelements: boron, manganese, uranium and rare earths, went into the fourth vessel. Distilled water was then again added up to a special mark. One pea plant was then stood in these four vessels placed side by side, after it had been cultivated on a net in tap-water.

Plants, 3—4 cm in height and with 8 approximately equal rootlets (7—8 cm long), were selected for planting. Every two rootlets were passed through one of four specially made holes in a wooden stopper. The rootlets were then placed together with the stoppers into separate vessels with the nutrient mixture and left there till the end of the experiment. Plants grown in solutions containing all the nutrient salts together were used as controls.

The tests were repeated three times. The plants were stood in the vessels July 30, 1935 and were harvested September 5, 1935, after the pods had formed.

It is interesting to note that up to the moment of flowering the pea plants in the vessels with isolated feeding showed as good a development as those in the control vessels. They only began to lag behind in growth after August 20.

The question is why did the plants in the vessels with isolated feeding lag behind in growth?

This is due to the fact that the roots of the plants could only develop in that vessel which contained calcium nitrate. In the remaining vessels the roots of the plants had hardly increased their initial size.

This is clearly demonstrated by the second experiment with pea and maize made in 1936 after the same method and scheme as in 1935, the only difference being that calcium bicarbonate was added to the two parallel vessels containing calcium phosphate, and magnesium sulphate and iron citrate respectively.

The result was that the weight of the root mass and the yield were the same in the vessels with $Ca(HCO_3)_2$ as in those containing all the nutrient substances together.

Experimental scheme	Mean weight of 1 plant in grams (dry weight). Pea			Mean weight of dry roots in the vessel with isolated feeding (separately)			
	Stalks	Pods	Roots	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	Fe citr.
Control (all the elements introduced together) . .	2.1	0.55	0.26	—	—	—	—
Isolated feeding without $Ca(HCO_3)_2$	1.32	—	0.13	0.016	0.070	0.013	0.012
Isolated feeding with $Ca(HCO_3)_2$	2.25	0.65	0.26	0.034	0.078	0.033	0.028

In the vessels containing no calcium bicarbonate the weight of the stems and of the roots is lower throughout. Analogous results were obtained with maize.

It should, however, be kept in mind that, in addition to calcium, plants need other nutrient substances as well in building up plant tissue. The specific peculiarity of calcium only more markedly manifests itself here.

The results of our experiments, thus, show that plants can develop and assimilate nutrient substances likewise in those cases where not only one

but all the four nutrient salts are administered separately. This, therefore, refutes the erroneous conception of the toxicity of pure nutrient salts for plants, which still persists in science. Professor N. Maksimov ([8]) writes: «If we were, for instance, to divide the roots of a plant into four strands, immersing each strand separately n one of the four salts that constitute Knopf's solution, we should poison the plant instead of supplying it with normal nourishment, and it would perish». This statement is obviously erroneous.

Now, what are the phemonena observed by Loeb and other investigators due to, and what is the essence of the so-called antagonism of ions? The answer runs as follows: each nutrient element retards the development of vegetable and animal organisms if its content in the nutrient mixture does not suffice for their normal needs, i. e. for the formation of some definite constituent requiered by plants and animals for building up their organism. And if one or several of the nutrient elements necessary for the growth of plants or animals are absent, then evidently no such growth can occur. Under such conditions, they will inevitably perish, though not from any toxic effect of the salts present, but from lack of the nutrient elements necessary for their development. Sea water is for marine animals as much of a nutrient medium as air and the nutrient substances of the soil are for plants.

The normal growth of plants and marine animals in equilibrated solutions is not due to the salts neutralizing their respective toxic effects but is due to such solutions supplying the necessary quantities of all the nutrient substances they require.

The essence of the physiological antagonism of ions must, consequently first of all be considered from the standpoint of the physiological significance of each nutrient element. This complicated biological process must not be fully reduced to physico-chemical phenomena occurring between the different ions of the electrolytes. Otherwise, we shall only make this most complicated physiological phenomenon still more obscure, instead of elucidating it.

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16. VIII. 1937.

REFERENCES

[1] П. Р. Слезкин, Изв. Петр. с.-х. Академии, 15—95 (1893). [2] П. Р. Слезкин, Журн. сельск. хоз. и лесоводства (1895). [3] И. Шулов, Исследования в области физиологического питания высших растений при помощи методов изолированного питания и стерильных культур (1913). [4] М. И. Сидорин., Из результатов вегетационных опытов, XI, 57 (1918). [6] М. К. Домонтович, Из результатов вегетационных опытов, XII (1923). [7] Д. Н. Прянишников, Юбилейный сборник, 2, 484—491. [8] Н. Максимов, Краткий курс физиологии растений для агрономов (1931).

PLANT PHYSIOLOGY

THE INFLUENCE OF THE RADIOACTIVE ELEMENTS URANIUM, RADIUM, THORIUM AND ACTINIUM ON THE YIELD OF PLANTS

By A. A. DROBKOV

(Communicated by D. N. Prianishnikov, Member of the Academy, 19. VIII. 1937)

The part played by the radioactive elements in the life of plants, the content of these elements in plants and their influence on the yield—are new problems which have been as yet but little studied. At the same time these problems are of great practical and theoretical importance, for the radioactive elements belong to the most widespread elements in nature, although they occur in a state of extreme dispersion. They are invariably

present in all soils, in all natural waters, in all plant and animal organisms, as has been demonstrated by the works of Academcian V. I. Vernadsky, K. G. Kunaševa, B. K. Brunovskij, Tomasin, A. Cann, A. Nodon, Zepape, S. Stoklasa, etc.

The vegetative experiments (water cultures) conducted by us in 1932, 1935 and 1936, for the purpose of studying the influence of uranium, radium, thorium and actinium on the yield of plants (pea and salad), and accompanied by determinations of the content of these elements in the plants, gave positive results in a number of cases, but only when the dosages remained within definite limits*.

Table 1, given below, summarizes the results of our experiments with radium (the Zhegalovski pea variety). That table shows the great sensitivity of plants to such extremely minute doses of radium, as, for instance, 10^{-11} g of radium in each vessel containing 6 l of distilled water.

In comparison with the controls (cultivated on Hellrigel's mixture $+B_{10,0}$) the above dosage increased the yield of vegetative mass by 86.27% and of pea seeds by 182.35%. This dosage is the optimum for vegetative mass, whilst the optimum dosage for seeds is ten times greater, namely, $1 \cdot 10^{-10}$ g of radium per vessel.

The yield both of vegetative mass and of pea seeds shows a gradual decrease with further successive increases of the radium dose (tenfold, 1.10^{-10}; a hundredfold $1 \cdot 10^{-9}$; and a thousandfold, $1 \cdot 10^{-8}$). In these experiments, however, we did not attain the lethal dose of radium for plants.

Table 1

The Influence of Radium on the Pea Plant

Scheme	Mean weight of dry stalks		Mean weight of dry seeds		Mean weight of dry roots	
	g	%	g	%	g	%
Hellrigel's mixture	2.80	57.37	—	—	0.50	89.28
» » $+B_{10}$	4.88	100.00	0.85	100.00	0.56	100.00
» » $+B_{10}+Ra\ 10^{-11}$.	9.09	186.27	2.40	282.35	1.00	178.75
» » $+B_{10}+Ra\ 10^{-10}$.	8.27	169.46	2.59	304.70	0.98	175.00
» » $+B_{10}+Ra\ 10^{-9}$.	8.72	158.38	2.02	237.64	0.85	151.78
» » $+B_{10}+Ra\ 10^{-8}$.	7.40	154.64	2.37	278.32	0.90	160.71

Table 2 shows how the content of radium in the plants changes with modifications in the radium concentration of the nutrient medium. An examination of the table shows at a glance that the radium content of the plants rises with increasing dosages of it in the medium. It is also noteworthy that the roots contain much more radium than the stalks.

Table 2

Experimental scheme	Content of Ra in the pea in percentages	
	In the stalks	In the roots
Hellrigel's mixture $+B+Ra\ 10^{-11}$	$5.02 \cdot 10^{-12}$	$1.19 \cdot 10^{-11}$
» » $+B+Ra\ 10^{-10}$	$1.96 \cdot 10^{-12}$	$1.46 \cdot 10^{-10}$
» » $+B+Ra\ 10^{-9}$	$3.37 \cdot 10^{-11}$	$1.45 \cdot 10^{-9}$
» » $+B+Ra\ 10^{-8}$	$5.07 \cdot 10^{-10}$	$1.04 \cdot 10^{-8}$

* In 1936 this work was being carried out in cooperation with the Biochemical Laboratory of the Academy of Sciences of the USSR. K. G. Kunaševa, B. K. Brunovskij and V. I. Baranov participated in the work.

Analogous data were obtained in respect of uranium, thorium and actinium.

Our three-years' experiments, therefore, enable us to draw the following conclusions: the radioactive elements (uranium, radium, thorium and actinium) are neither stimulants nor catalyzers, as is the common opinion, but are as necessary nutrient substances as boron, manganese and other microelements. The only difference is that the plant requires only infinitesimal amounts of them.

The radioactive elements, evidently, play an important physiological role in plants.

The great importance of radioactive elements in the life of living organisms is confirmed by the somewhat indirect fact that these elements occur in considerable concentrations in products of organic origin, which date back to the geological past, as coal, phosphorite, etc.

The question of whether the radioactive elements can replace each other, or whether each of them fulfils a definite and specific physiological role, is as yet unsolved. At present the following two points may be considered established:

1) The radioactive elements: uranium, radium and thorium, cannot be used as substitutes for other nutrient elements.

2) Potassium, notwithstanding its radioactive properties, cannot replace the other radioactive elements.

This is important from the point of view of practice; for it becomes increasingly obvious that under natural conditions the volume of the harvest does not only depends on the presence in the soil of definite quantities of nitrogen, phosphorus and potassium (as we are wont to think), but also on an adequate supply of microelements; in particular, on the presence in the soil of sufficient quantities of radioactive elements.

It is true that at present no due attention is paid to this question either in the theory or in the practice of fertilization. But the lack in radioactive elements may be remedied to a considerable extent by their introduction into the soil together with organic and mineral fertilizers, where they are constantly present as admixtures. Thus, for instance, V. K. Rusanov's study of 49 samples of phosphorites from the Western Territory showed them to contain $31 \cdot 10^{-4}$ uranium units of radioactive elements.

On the other hand, the soil contains fairly high amounts of radioactive elements as compared with the requirements of plants. The radium content in the soil is, for instance, in the neighbourhood of $1 \cdot 10^{-10}\%$. Consequently, one hectare of arable soil and subsoil, to a depth of 40 cm (assuming the weight of this layer to be $6 \cdot 10^6$ g), will contain about $6 \cdot 10^{-3}$ g of radium.

The yearly absorption of radium out of the soil by high yields (100 t of dry matter per hectare) totals $1 \cdot 10^{-6}$ g per hectare (assuming tentatively the radium content in plants to be about $2 \cdot 10^{-12}\%$). The amount of radium contained in the soil is therefore about 3 000 times as great as that required by plants. But we do not yet know what quantities of radium are available for plants.

It may be well to mention that an essential defect of former experiments, carried out mainly with radium, was that the dosages of radium administered by the majority of investigators were too high, being a thousand times as great as the optimum concentration. This explains the great discrepancies in the results obtained. Thus, for instance, Stoklasa, Akva, Molisch and Baker obtained positive effects of radium on the yield of a number of crops potatoes, tomatoes, wheat, peas, beet, etc.; whilst in the experiments made by Cymmona, Wallace, A. Stona and Zepape, the radium produced no increase in the yield.

There were no precise physiological experiments, which could give a notion of the optimum concentrations for plants of radium and other radioactive elements. This was first carried out by us.

In conclusion it is necessary to answer the question why some investigators both formerly and now frequently succeeded in growing normal plants in distilled water to which only seven elements had been added.

The following answers to these questions may be suggested:

1. The nutrient salts introduced usually contain admixtures of microelements, which, as a rule, is not taken into account.

2. The distilled water used in water cultures is not pure enough, this is clearly confirmed by our experiments, which will be dealt with in a separate paper.

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19. VIII. 1937.

REFERENCES

[1] V. I. Vernadsky, C. R. Acad. Sci. URSS, № 2 (1929). [2] Б. Бруновский, Тр. Биогеохим. лабор. Ак. Наук, II (1932). [3] Б. Бруновский и К. Кунашева, Тр. Биогеохим. лабор. Ак. Наук, III (1935). [4] S. Stoklasa, Biologie des Radiums und der radioactiven Elemente (1931). [5] B. Rusakov, C. R. Acad. Sci. URSS, № 10 (1931). [6] A. Nodon, C. R., 178 (1924). [7] A. Cann, Biochem. ZS., 11 (1911). [8] В. И. Вернадский, Очерки геохимии (1934). [9] Э. Рассель, Почвенные условия и рост растений (1931).

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ZOOLOGY

NEW SPECIES OF *OLIGOCHAETA LIMICOLA* IN THE EUROPEAN PART OF THE USSR

By D. A. LASTOČKIN

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Eleven species of *Oligochaeta limicola* have been discovered as yet only in the European part of the USSR: *Acolosoma neizwestnovae* Last., *Potamodrilus stephensoni* (=*Stephensoniella fluviatilis*) Last., *Chaetogaster setosus* Svetlov, *Nais behningi* Mchlsn., *Vejdovskyella macrochaeta* Last., *Ripistes rubra* Last., *Dero michaelseni* Svetlov, *Pristina amphibiotica* Last., *Tubifex* (*Tubifex*) Smirnovi Last., *Limnodrilus newaensis* Mchlsn. and *Lamprodrilus isoporus* f. *variabilis* Svetlov. According to this preliminary account, the number may be almost doubled.

Among the river fauna, *Limnodrilus michaelseni* and *Chaetogaster krasnopolskiae* have been found. Both these species are characterized by the reduction of the upper prong of their setae (a common feature of the sand-benthos *Oligochaeta*) and by a simplified structure (in comparison with closely related species) of the vascular system.

Fig. 1. Genital seta of *Limnodrilus michaelseni* n. sp.

Limnodrilus michaelseni n. sp. has funnel-shaped anterior setae, ventral crotchets of IX—XII segments are replaced (Fig. 1) by single gential setae with a strongly developed upper prong (in spite of its reduction in all other bundles) and a lower prong perpendicular to the setae axis. Length of worm, 26—28 mm; number of segments 110; length of ventral crotchets, from 72 to 118 μ, of dorsal crotchets, from 69 to 114 μ; genital setae, 125—145 μ. Penis tubes are absent. Widely distributed in rivers, found in the Caspian Sea and the Nieva bay of the gulf of Finnland.

Chaetogaster krasnopolskiae. Length of chains, 1.2—1.4 mm; length of zooids, 0.65—0.8 mm. Length of crotchets, from 60 μ (II segment) to 51 μ, $n=8$. The oesophagus is twice as short as the pharynx. The oesophageal vascular ring is absent; ventral vessel in its upward course along one side of the oesophagus passes into the dorsal vessel; pharyngeal vessels are absent. There is no chitin plate in the cerebral ganglion. Occurs in the Volga, the Moskva and the Dnieper.

In the Caspian Sea two new species have been discovered: 1) *Tubifex* (*Psammoryctes*) *deserticola* Grimm, which used to be considered doubtful, is now quite established (only maturing specimens have been found). It

is closely related to the *Tubifex* (*Psammoryctes*) *ochridanus* Hr., but is distinguished from the latter both by the shape of ventral and dorsal crotchets and by its nephridia. The latter occur only on the left side and are characterized by a large (70×46μ) terminal dilatation opening directly in front (16—20μ) of the ventral crotchet; 2) *Ilyodrilus caspicus* n. sp. belongs to that group of species of this genera the dorsal crotchets of which are similar to their ventral crotchets, whose hair setae are either absent or occur only in the postclitellar segments (*Ilyodrilus isochaetus*, *moldavensis*, *praespensis*, *ochridanus*).

The new species has no hair setae and all the crotchets have prongs of the same shape 80—130 μ long. The atrium forms a loop directly after the aperture of a small prostale, continues in a horizontal direction and finally forms a second, usually more intricated, loop before passing into the penis, whereas the atrium of other species consists of two horizontal parts joined behind by a genicular bent. The genital setae are single and in shape and size scarcely distinguished from common ventral crotchets.

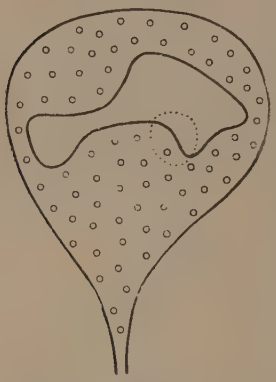

Fig. 2. Nephridial (?)cell of *Tubificoides heterochaetus* n. g. n. sp. (ocul.—12 compens, obj.—4 mm).

The worm consists of about 130 segments, 26 mm long.

Tubificoides heterochaetus n. g. n. sp. from the oligohaline lakes in the mouth of the Kuban river. This worm is about 20 mm long and has 65 segments. Ventral crotchets (about 60 μ long) have everywhere two prongs, same as the dorsal preclitellar crotchets. Postclitellar dorsal setae are blunt-point needles, similar to those of *Nais simplex*. Hair setae are of the same type, but 1.5—2 times as long (94—115 μ). Remarkable is the entire absence of nephridia; evidently instead of them there are large cells with a considerable vacuole (Fig. 2) disposed in single file in the middle segments at the posterior septa. Structure of genital system is of the type of *Tubifex* with a complex atrium (flat darkly pigmented cells in the ental part, cubic cells with reticulated protoplasma in the middle part and granulated cells of average size in the ektal part). Vas deferens is longer than atrium by 1.5—1.7. A well developed penis. Large glands are disposed medio-ventrally in XI and XII segments.

In the Coporskaya bay of the Gulf of Finnland, Mrs Ioffe discovered a new species which I describe below under the name of *Spiridion scrobicularae* n. sp. It is distinguished from *Spiridion insigne* by the presence of an unpaired medial genital cavity into which open both the atriums and the groups of penial setae. The atrium is muscular and unciliated and consists of a narrow anterior part and a pear-shaped posterior part. The atrium at its very end receives the secretion of a rather large gland. The clitellum is rudimentary and develops only in the region of the spermathecal apertures and in the region of the genital cavity.

In Umbosero (Soviet Lappland) a fauna has been found that bore a striking resemblance to that of Swedish Lappland, but here, instead of the Swedish species *Rhyacodrilus ekmani*, a special variety occur—var. *profundalis*. The variety is distinguished from the original species both by the size of the setae (ventral crotchets are longer by 23—33 μ; dorsal crotchets, by 19—43 μ, and hair setae, by 60—100 μ) and by the dorsal crotchets having a fine membrane between the prongs. All the crotchets distinctly possess a characteristic broadening of the distal part of the setae («hunched»

setae). The spermathecae are not connected with the intestine. The new variety is to be found only at a depth of 50—98 m.

In the Crimea, a wonderful discovery has been made by me of a representative of the American genera *Mesoporodrilus*. As far as I am not acquainted with the work of Smith (1919), I am unable to decide whether this species is a new one or whether it is identical with *Mesoporodrilus lacustris*.

Finally, in the Dnieprogess water reservoir, M. F. Jaroschenko and I discovered two new species of *Ilyodrilus*. One of them *Ilyodrilus swirenkoi*, possesses the same peculiarities as the above-described group of species belonging to this genera, i. e. large size (38 mm), great number of segments (180), great number of crotchets (4—7 dorsal and 5—8 ventral crotchets) and the absence of denticles between the prongs of the dorsal crotchets. The atrium is constructed after the type characterized by two joined horizontal parts.The genital setae are similar to those of *Ilyodrilus heuscheri*, but in this case they are twice as short and twice as thin, they end straight and have no prong. But the principal distinction of the new species lies in its setae. The crotchets are very short and have a distinct curve in the distal part of dorsal crotchets, they have a rudimentary upper prong. The hair setae are absent in preclitellar segments, only, from XV segment they begin to appear as single, very fine, very brittle and extremely long setae (in LXII segment 1002.5μ long)*. The other new species of *Ilyodrilus* will be described by M. F. Jaroschenko. The South-Fast of Europe is an important species-forming centre for this genus, where six out of eleven species of this genus were found (three are mentioned in this account, the other three are described by Hrabje in Jugo-Slavia).

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REFERENCES

[1] Hrabje, Zoologische Jahrb., 64 (1931). [2] Smith, Proceed. biolog. Soc. Washing., 32 (1919).

* By its curved dorsal crotchets and by its exceptionally long hair setae, this new species bears a remarkable resemblance to *Tubifex* (*Tubifex*) *fillum* Mchlsn.

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MATHÉMATIQUES

LA SUBSTITUTION EXPONENTIELLE POUR UN SYSTÈME IRRÉGULIER D'ÉQUATIONS DIFFÉRENTIELLES LINÉAIRES

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Prenons un systéme irrègulier d'équations différentielles linéaires:

$$\frac{dY}{dx} = Y \sum_{P=-S}^{\infty} T_P x^P \qquad (S > 1), \tag{1}$$

où Y est une matrice intégrale, les matrices T_P ne dépendent pas de x, et la série considérée est convergente au voisinage de $x = 0$. La matrice intégrale normalisée au point $b\,[Y(b \mid x) = I]$ peut être représentée dans la forme $Y(b \mid x) = x^{W(b)}\overline{Y}(b \mid x)$, où la matrice $\overline{Y}(b \mid x)$ est uniforme au voisinage de $x = 0$ et $W(b)$ est une substitution exponentielle de la matrice $Y(b \mid x)$.

Si $V(b)$ est une substitution intégrale, s'est-à-dire la matrice $Y(b \mid x)$ reçoit de côté gauche le multiplicateur $V(b)$ quand x tourne autour de $x = 0$, alors

$$W(b) = \frac{1}{2\pi i} \lg V(b). \tag{2}$$

La matrice $V(b)$ est une fonction entière T_P* (v. I, p. 233). La relation entre $W(b)$ et T_p est d'un caractère plus compliqué. Dans la suite nous verrons que c'est une fonction à un nombre infini des branches.

Si X est une matrice quelconque, alors d'après la formule de Sylvestre:

$$Z = \lg X = \alpha_{n-1} X^{n-1} + \alpha_{n-2} X^{n-2} + \ldots + \alpha_0, \tag{3}$$

où α_k sont des fonctions rationnelles de x_i et $\lg x_i$, où x_i $(i = 1, \ldots, n)$ sont des nombres caractéristiques de X. α_i peut être déterminé par le système des équations linéaires

$$\sigma(X^l Y) = \alpha_{n-1}\sigma(X^{l+n-1}) + \alpha_{n-2}\sigma(X^{l+n-2}) + \ldots + \alpha_0\sigma(X^l) \qquad (l = 0, 1, \ldots, n-1), \tag{4}$$

où l'on désigne par $\sigma(U)$ la trace de la matrice U.

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À l'aide de la formule $\lg x = \int_0^1 \frac{x-1}{1+t(x-1)}\,dt$ nous obtiendrons:

$$\sigma(X^l Z) = \int_0^1 \frac{\sum_{k=1}^{l+1}\sum_{P=0}^{n-1} \frac{l(l-1)\dots k}{(l-k+1)!}\, t^P A_P^k}{\sum_{P=0}^{n} t^P S_P}\,dt, \qquad (l=1,\dots,n-1), \tag{5}$$

où les S_l sont des fonctions symétriques élémentaires de $(x_i - 1)$ et les A_P^k sont des polynomes de S_l. En particulier $\sigma(Z) = \lg D(X)$, où $D(X)$ est le déterminant de la matrice X. En résolvant le système (4) nous obtenons:

$$\alpha_i = \frac{\Delta_i}{\Delta(X)} \qquad (i=0,1,\dots,n-1), \tag{6}$$

c'est-à-dire:

$$Z = \lg X = \frac{\Delta_{n-1}X^{n-1} + \Delta_{n-2}X^{n-2} + \dots + \Delta_1 X + \Delta_0}{\Delta(X)}. \tag{7}$$

En applicant ses résultats à la fonction (2) nous n'obtenons pas une représentation locale, mais une représentation g é n é r a l e de $W(b)$.

$$2\pi i W(b) = \frac{\tau_0 + \sum_{\nu=1}^{\infty}\sum_{P_1\dots P_\nu=-s}^{\infty} T_{P_1}\dots T_{P_\nu}\tau_{P_1\dots P_\nu}}{\Delta(V(b))}, \tag{8}$$

où les τ dépendent linéairement des Δ_i et au lieu de S_l nous pouvons prendre $\sigma(V^k)$ qui sont des fonctions entières de T_P (v. I, p. 233). Si l'on prend les systèmes d'équations du second ordre où $T_{-1} = 0$, alors $D(V) = 1$, $\sigma(W) = 0$ et toutes les déterminations multiples de $W(b)$ sont contenues dans la fonction (5) quand $l = 1$. Dans le cas du système:

$$\frac{dY}{dx} = Y\left[\frac{\alpha\begin{Vmatrix}0 & 0\\ 1 & 0\end{Vmatrix}}{x^2} + \frac{\beta\begin{Vmatrix}0 & 1\\ 0 & 0\end{Vmatrix}}{x+1}\right], \tag{9}$$

où α et β sont des paramètres; la fonction mentionnée sera:

$$\Phi(z) = \sigma(VW) = \frac{z^2-4z}{2}\int_0^1 \frac{dt}{t^2z - tz + 1},$$

où $z = 2 - \sigma$ et $\sigma = \sigma(V) = -2\cos\pi\sqrt{1+4\alpha\beta}$.

Si z tourne autour de $z = 4$ la fonction $\Phi(z)$ augmente de $\frac{2\pi i}{\sqrt{z(z-4)}}$ et un second tour la réduit à sa valeur initiale. Nous aurions pu obtenir une infinité de valeurs si avant de tourner une seconde fois autour de $z = 4$ on aurait fait un nombre impair de tours autour de $z = 0$; mais d'après les formules σ il est évident que chaque contour fermé dans l'espace des paramètres complexes α et β donne un nombre pair de tours autour de $z = 0$, et, par conséquent, pour le système (9) $W(b)$ est une fonction à deux valeurs de α et β.

Nous obtiendrons une $W(b)$ à une infinité de valeurs pour un système plus général à quatre paramètres:

$$\frac{dY}{dx} = Y\left[\frac{\begin{Vmatrix}\gamma & 2\gamma\\ 4\gamma+\alpha & 3\gamma\end{Vmatrix}}{x^2} + \frac{\begin{Vmatrix}\tau & \beta-\tau\\ 0 & 2\tau\end{Vmatrix}}{x+1} + \begin{Vmatrix}0 & 0\\ 0 & -2\tau\end{Vmatrix}x\right].$$

La trace $\sigma(V)$ ne dépend pas du choix de la matrice intégrale Y et en utilisant la matrice métacanonique (v. I, p. 249) nous aurons:

$$\sigma(V) = -2\cos\pi\sqrt{1+4\alpha\beta} + \psi(\gamma, \alpha, \tau, \beta) + \varphi(\gamma, \tau)$$

où ψ et φ sont des fonctions entières, $\psi(0, \alpha, 0, \beta) = \psi(\gamma, 0, \tau, 0) = 0$ et $\varphi(\gamma, \tau) = \gamma^3(m \cdot \tau^3 + 576\pi^2\tau^2) + \gamma^4\omega(\gamma, \tau)$.

En ce cas en faisant le tour de quelques contours fermés dans l'espace des paramètres, on peut faire le tour de $\sigma = -2$ une fois, et de $\sigma = 2$ trois fois, ce qui démontre que W a une infinité de branches.

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